

Laser Ablation in Atomic Spectroscopy

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Laser ablation (LA) is a unique technique to transform a solid sample into vapor-phase constituents, which then can be chemically analyzed by atomic spectroscopy. Ablation brings many exciting capabilities to the field of chemical analysis, primarily because of the laser-beam

properties. The ability to analyze directly any solid sample without sample preparation and minimal sample-quantity requirements are just some of the unique capabilities. This article discusses current issues related to using LA in atomic spectroscopy. A general introduction to LA sampling is presented along with a comparison with other solid sampling techniques. The critical issues for all analytical techniques are calibration, accuracy, and sensitivity. Techniques that have been demonstrated to address these analytical characteristics and define these parameters for LA are investigated in detail. Finally, many unique applications are described, ranging from dating geological materials to providing crime-scene evidence. Most of these applications could not be performed without the use of a laser beam. The inductively coupled plasma (ICP) will be emphasized in this article because it is currently the most prevalent excitation and ionization source for chemical analysis using LA.

1 INTRODUCTION

Want to know the composition of an unknown solid sample? Don't want to deal with acids, wastes, and laborious procedures to conduct the analysis? What is the best way to transform the unknown solid sample into vapor-phase constituents for chemical analysis? The answer: explode the sample with a high-power laser beam! This is precisely the role of LA in atomic spectroscopy. Complex solid samples, including environmental wastes, geochemical materials, coatings, extraterrestrial samples, and others dictate the development of a sampling approach for chemical analysis that does not rely on complicated, laborious dissolution procedures; a direct approach for analyzing unknown samples has been a quest of analytical chemistry for a long time. In some cases, the desire is to analyze a sample chemically without destruction, especially if that sample is the Shroud of Turin! These are some of the characteristics that make ablation sampling attractive for atomic spectroscopy.

This article will discuss current issues related to LA in atomic spectroscopy, including calibration and optimization, accuracy, sensitivity, and particle transport. In addition, many unique applications will be described, in some cases applications that cannot be performed without the use of a laser. The ICP is emphasized in this article because it is the most prevalent excitation and ionization source for chemical analysis using LA at this time.

1.1 Characteristics of Laser Ablation

One of the most unique characteristics of LA is that any solid sample can be directly ablated into vapor-phase constituents (vapor and particles), be it a rock,

hair sample, extraterrestrial sample, or priceless piece of artwork. Only a very small portion of the sample is required for the analysis – sometimes of the order of picograms or less. Damage at these levels is generally not visible without the use of a microscope. In addition, there is no requirement for sample preparation; the laser beam can be used to ablate the surface contamination, as well as dig a crater and provide bulk analysis.

Because the laser beam directly converts the solid sample into the vapor phase, liquid reagents are not required to digest the sample. Therefore, there is no solution waste, no worries about loss of volatile species, and minimal sample handling. In addition, when liquid sample introduction is used, a larger portion of the sample is required because of dilution. Another significant and unique advantage of LA is the ability to perform spatial (micrometer) characterization. Since the laser beam can be guided to an exact location on a surface, the analyst can choose where the explosion and, therefore, the sampling occur. If the sample of interest is the microscopic inclusions in a bulk material, or particles on a filter paper, it is not necessary to analyze the entire sample; most of the mass in this case is not related and leads to large background signals in the analytical source. Finally, if one wants the analysis performed immediately, LA is the way to go – there are no time-consuming sample preparation or dissolution procedures; just place the sample in a simple chamber and hit it with the laser beam. With capabilities and advantages such as these, LA atomic spectroscopy is now utilized routinely in many industries, using commercially available and laboratory-built systems.

1.2 Solid Sampling Techniques: Comparison

The development of any “new” technique for elemental analysis requires parameters such as sampling, excitation, ionization, and detection to be critically investigated and optimized. An “ideal” sample introduction technique has to satisfy certain criteria, which include:

- remove a sufficient quantity of sample;
- reproducible sampling;
- minimal interference on the performance of the detection system;
- sampled material must be representative of the bulk composition (stoichiometry);
- absence of matrix effects (no variation of analyte signal in different matrices);
- sample transport to the excitation or ionization source without losses;
- absence of memory effects and sample carryover;
- adjustment of sampling parameters to satisfy detection requirements.

Among the most popular direct solid sampling methods are LA, glow discharge (GD), and spark/arc ablation. Direct analysis of solids with GD sources has been used with both atomic emission and mass spectrometric detection. GD converts a solid sample directly into the atomic phase by sputtering processes. Because sputtering is a primary sampling mechanism, heating is minimal and preferential vaporization is minimized. GD is best suited for conductive samples, although nonconductive samples can be analyzed with a radiofrequency discharge. A GD source coupled to a high-resolution mass spectrometer is a powerful technique for achieving excellent depth profiling and detection characteristics with a limit of detection (LOD) in the range 10–100 ng g⁻¹.

For arc/spark ablation, mass is eroded from the sample in the form of atoms, molecules, vapor, droplets, solid flakes, and large particles. Normally, only conductive samples can be used with a spark discharge; however, nonconductive materials can be analyzed by mixing the sample with a conductive matrix.

Because of unique benefits and capabilities for direct solid sampling, LA has outpaced development of these other techniques. Laser sampling has been employed with flame and graphite furnace atomic absorption spectroscopy, with typical LODs in the micrograms per gram range. A description of these methods can be found in a review by Darke and Tyson.⁽¹⁾ The direct current plasma (DCP) and microwave-induced plasma (MIP) have been used for the analysis of solid samples with LA sampling.^(2,3) The DCP and MIP offer good detection limits in the micrograms per gram range, with linear calibration curves over several orders of magnitude of concentration.

The ICP has become the prevalent source for chemical analysis with LA sampling.⁽⁴⁾ The ICP plasma is robust, with high temperature and electron number densities, and is in most cases unperturbed by small amounts of sample. A separate article (**Inductively Coupled Plasma/Optical Emission Spectrometry**) is dedicated to the ICP. Slurry nebulization of powders, electrothermal vaporization (ETV), direct sample insertion (DSI), spark/arc and LA techniques are among the most popular methods investigated for solid sampling into the ICP. Each of these techniques has unique features: sensitive analysis of powders (slurry nebulization, ETV); analysis of small volumes of solids and liquids with selective solvent or matrix removal (ETV); direct sampling and atomization in the ICP plasma (DSI); analysis of conductive samples (spark ablation); and analysis of any sample (LA). A comparison of slurry nebulization, ETV, and LA methods was reviewed by Darke and Tyson.⁽⁵⁾ DSI for ICP was recently reviewed by Sing.⁽⁶⁾

2 FUNDAMENTAL CHARACTERISTICS

Because of the numerous capabilities and advantages for atomic spectroscopy, there is a tremendous demand to understand fundamental LA processes. LA is complex, consisting collectively of many nonlinear mechanisms, each operative on different timescales, from femtoseconds to seconds. When the laser beam irradiates the surface, electrons will be released on the femtosecond to picosecond timescales, followed by atomic and molecular mass on the nanosecond timescale, and then the eruption of large particles, microseconds after the laser pulse has ceased (Figure 1a–c). With different processes occurring over so many orders of magnitude in time, it is no wonder the collective phenomena have never been combined into a unifying theory. However, it is critical to point out before discussing fundamental issues that LA sampling is easier than liquid nebulization. In fact, there have been many years of science devoted to proper dissolution procedures in order to achieve accurate analysis – and still one must be very careful when dissolving a sample that is truly ‘unknown’. The underlying fundamentals of LA should not preclude its development as the method of choice for direct solid sampling in atomic spectroscopy.

Studying fundamental LA mechanisms will provide further improvements and benefits for atomic spectroscopy. By understanding ablation, it will be possible to control process variables, such as the ability to couple the laser beam efficiently into the sample, ablate a reproducible quantity of mass, control the amount of mass ablated, minimize preferential ablation, produce stoichiometric ablation, and control the particle size distribution. By controlling these variables, LA in atomic spectroscopy will become a routine chemical analysis technology for environmental, health, forensics, nonproliferation, and other applications where the primary sample is in the solid phase.

2.1 Ablation Processes

Many studies have been dedicated to understanding fundamental ablation mechanisms. Research studies have shown that LA of a solid sample consists of several stages, in which different kinds of ‘vapor products’ are ejected. The initial stage is electronic excitation inside the solid, accompanied by ejection of electrons at the sample surface, due to both photoelectric and thermionic emission. During this time, energetic electrons in the bulk of the solid also transfer energy to the lattice through a variety of scattering mechanisms; the sample target then undergoes melting and vaporization, followed by ionization and formation of a plasma plume consisting of the sample constituents. The expanding plume interacts with the surrounding gas to form a shock wave, causing

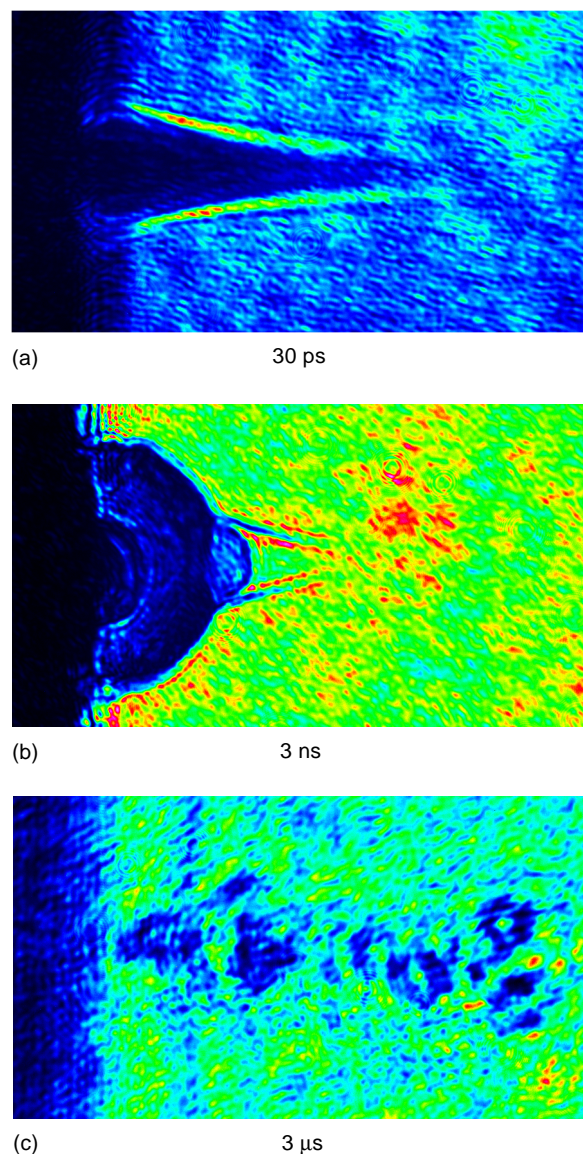


Figure 1 LA involves complex and collective phenomenon, exhibiting significant nonlinearity in space and time. The images show the evolution of the laser explosion from a solid surface. (a) At 30 ps after the laser hits the sample, electrons leave the surface and collide with air to form the plasma; (b) at 3 ns, atomic vapor escapes from the surface; and (c) at 3 μs, large (>20 μm) particles are spalled from the bulk.

the ambient gas to become further ionized. The expanding high-pressure plasma exerts a force back to the target, which flushes out the melted volume. This recoil pressure and flushing mechanism can produce large-sized particles (several micrometers). There is evidence of explosive boiling, occurring microseconds after the laser is finished, which also can produce micrometer-sized particles. Atomic- and micrometer-sized particles will both be transported to and digested in the ICP. Therefore, it

is important to understand mechanisms of atomic- and micrometer-sized particle generation; particles in each of these size ranges can have different chemistries, affecting analytical accuracy. The particle size distribution will also affect transport efficiency and therefore analytical sensitivity.

To achieve accurate LA sampling, the composition of the ablated mass should be the same as the sample composition. To achieve high sensitivity, all of the ablated mass should be transported to and digested in the ICP. There are four primary processes that influence the accuracy and sensitivity in laser ablation/inductively coupled plasma (LA/ICP). The first is the LA process itself. For different laser conditions, the composition and quantity of the ablated mass can change significantly. The particle size distribution and particle composition can also change with laser conditions. The second process is transport, which includes the sample chamber design and tubing used to carry the ablated mass to the ICP. Transport efficiency will be different for different sized particles. The third process is sample digestion and excitation in the ICP. The conditions in the ICP (electron temperature and number density) which are controlled by ICP power, gas flow rate, and height above the load coil will influence vaporization, atomization, and ionization of the analyte. However, the amount and composition of the analyte and the matrix can change the ICP conditions (Figure 2). The fourth process includes detection, using the mass spectrometer for inductively coupled plasma mass spectrometry (ICPMS) or the spectrometer and photon detector for inductively coupled plasma atomic emission spectroscopy (ICPAES). These processes are discussed separately below as to their influence on accuracy and sensitivity.

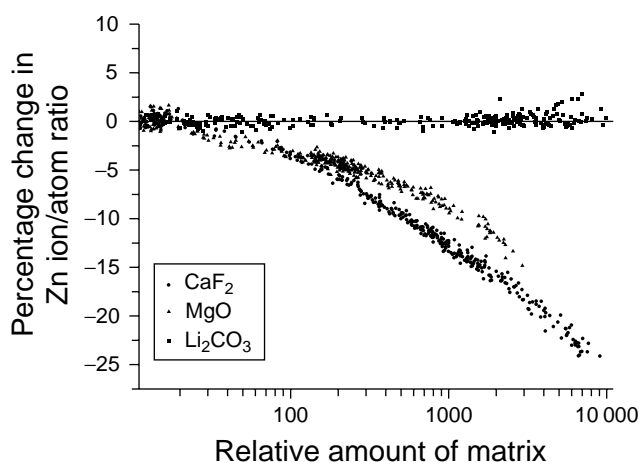


Figure 2 Percentage ratio change of Zn ionic to atomic emission lines in the ICP versus amount of matrix. The ratio of ionic to atomic line intensity correlates to the ICP conditions. LiF, CaF₂ and MgO were the matrices.

List of general abbreviations appears on back endpapers

2.2 Processes Affecting Accuracy

An expectation of any analytical procedure is accurate analysis; the detected mass composition must be the same as the sample composition. For LA sampling, fractionation (preferential mass removal during LA), which can cause inaccurate analysis, can occur under some conditions. Numerous studies have shown that fractionation can be minimized or eliminated, depending on the sample and laser properties.^(7–13) The distribution of elements in the matrix, their status (inclusions), and zone migration will influence fractionation.^(11,12) Fractionation at the sample is a function of wavelength; ultraviolet (UV) LA has been found to provide better stoichiometry than infrared (IR) LA.^(14–16) The number of laser pulses at a fixed location on the sample, the laser irradiance, and laser beam spot size (related to focus position) also influence fractionation (Figure 3).^(13,16,17) For fundamental purposes to describe fractionation at the sample, attempts have been made to correlate ablation behavior with melting, boiling, vapor pressure, atomic or ionic radius, charge, and speciation.^(1,15,18)

The mechanism for atomic mass ejection can be thermal vaporization and/or plasma sputtering. The sputtering process involves the high-temperature, high-pressure plasma colliding with the sample surface. The ablation rate in these two processes will depend on the bond energy; the stronger the bond, the less mass is removed. Fractionation on the nanosecond timescale can be related to thermal properties of the sample constituents. Fractionation in alloys depends on the latent heat of vaporization; the higher the latent heat, the more difficult it is to vaporize a constituent. For example, in brass, the latent heat of vaporization of Cu is greater than that of Zn;⁽¹⁰⁾ Zn can be preferentially ablated compared with Cu in these samples. By using a calibrated ICPAES instrument, fractionation based on thermal vaporization was demonstrated by measuring Zn/Cu mole ratios during ablation of brass. With a 30-ns, 248-nm excimer laser, the Zn/Cu mole ratio initially decreased with increasing laser irradiance, then stabilized at irradiance greater than approximately 0.3 GW cm⁻². The initial decreasing Zn/Cu ratio was due to thermal vaporization.⁽¹⁴⁾ For higher laser irradiance, there are likely several competing mechanisms involved in the ablation processes. Melt flushing from the crater, plasma shielding, and/or radiative heating by the laser-induced plasma can contribute to mass ejection.^(7,10,19,20) Picosecond LA is even more esoteric; nonthermal mechanisms must be operative. Using a 35-ps pulse (Nd:YAG, Nd³⁺:Y₃Al₅O₁₂) laser, some type of nonthermal mechanism appears to govern the LA process because Cu is enriched in the vapor at lower irradiance. The Zn/Cu ratio approaches the stoichiometric value at higher irradiance. These experiments demonstrate that different

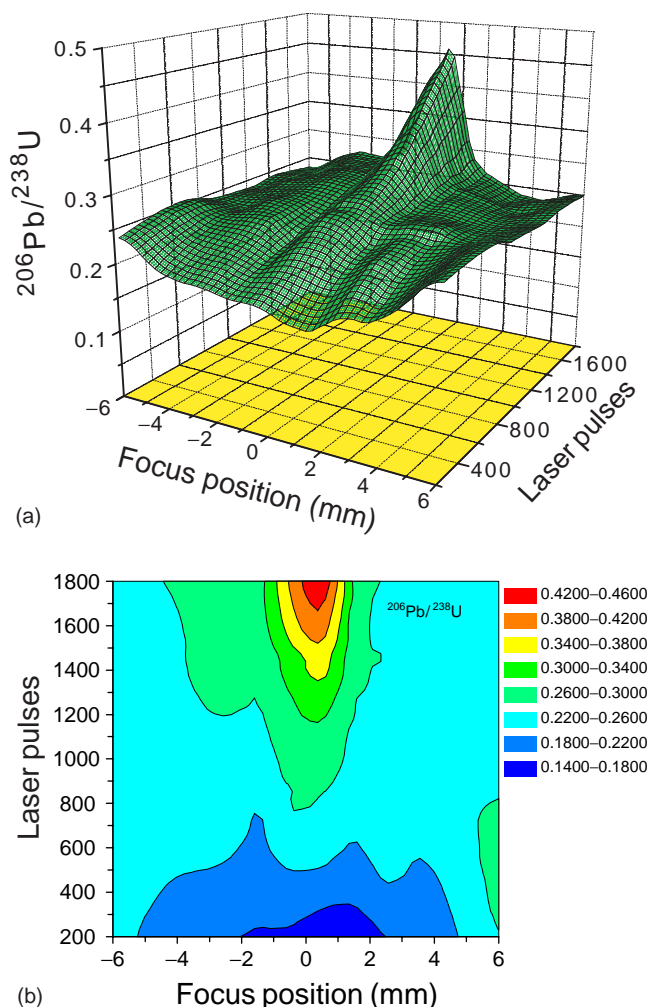


Figure 3 Pb–U fractionation versus number of laser pulses and lens-to-sample focal position: (a) three-dimensional plot; (b) contour plot. Neodymium:yttrium aluminum garnet (Nd:YAG) laser, $\lambda = 213$ nm; pulse duration = 6 ns; energy = 1.15 mJ; sample: NIST SRM 610 glass in which the $^{206}\text{Pb}/^{238}\text{U}$ stoichiometric ratio is 0.2249. The positive and negative values represent the laser focus above and below the sample surface, respectively.

mechanisms contribute to fractionation, although identification of the mechanisms is still a large research effort.

Fractionation during transport and/or in the ICP can occur.^(21,22) Fractionation during transport involves selective vapor condensation on the tubing walls or the selective nucleation of species on different-sized particles.⁽¹²⁾ These effects are governed by the vapor-phase morphology (droplet/particle shape and size) and chemical composition. Because transport efficiency and chemical composition are particle size dependent, fractionation can occur during transport. Figg et al.⁽²²⁾ demonstrated this effect by inserting a coiled Tygon tube into the transport path; both particle size distribution

and fractionation changed significantly. It is believed that many of the large particles come from flushing out the molten liquid layer. The composition of the molten liquid could be significantly different from the bulk because of preferential vaporization and re-deposition from the plasma plume. For “large” particles entering the ICP and undergoing sublimation (vaporization), fractionation may exist in the ICP itself.^(21,22) It is important to state here that fractionation is not a problem that precludes the use of LA for accurate chemical analysis, especially when matrix-matched standards exist. This section was designed to make the reader aware that such issues can exist. There are many applications of LA, as will be discussed in a later section, in which fractionation does not influence the analysis.

2.3 Processes Affecting Sensitivity

The signal intensity in atomic emission spectroscopy (AES) or mass spectrometry (MS) corresponds directly to the quantity of mass ablated and transported to the ICP. Depending on the concentration of the elements in the sample, it may be necessary to increase the quantity of ablated sample to achieve better signal-to-noise ratios. Laser-beam properties (such as wavelength, pulse duration, energy, fluence, irradiance, and temporal and spatial profiles) and the ambient gas influence the quantity of mass ablated per laser pulse.^(7,15,16,21,23–33)

2.3.1 Laser Energy

The ablated mass can be increased by increasing the laser-beam energy or fluence (energy per unit area). However, the relationship of ablated mass to laser-beam energy or irradiance is not linear;^(7,18,19,34) mass was found to follow a power law with irradiance (I^m).^(18,19,34) Using nanosecond laser pulses, with irradiance less than approximately 0.3 GW cm^{-2} , m had values ranging from 2 to 5 for many samples. When the irradiance was $>0.3 \text{ GW cm}^{-2}$, m became <1 . However, as the irradiance was increased further, another change in the mass ablation rate occurred, in which m increased to >2 . In the lower irradiance region, thermal vaporization was found to be a dominant process,⁽¹⁴⁾ as evidenced also by fractionation (discussed earlier). In the middle laser irradiance range, plasma shielding may be a major factor governing ablation. The laser-induced plasma formed above the target surface can absorb and/or reflect incident laser energy, thereby decreasing the efficiency of laser energy available for mass ablation.⁽³⁵⁾ A plasma can transmit just enough energy to the surface to sustain itself. The density and temperature of the plasma can adjust in such a manner that the optical thickness remains constant; the final proportion of the laser energy absorbed and transmitted is

constant. It is important to point out that this plasma is the basis of another chemical analysis technique, discussed in the article **Laser-induced Breakdown Spectroscopy**.

In the third irradiance region, mechanisms such as phase explosion and spallation may be dominant. Both crater depth and ICPMS intensity (Figure 4a–c) show dramatic increases at a threshold irradiance of $20\text{--}30\text{ GW cm}^{-2}$. This dramatic change may be caused by explosive boiling.⁽³⁶⁾ The superheated molten liquid can experience an increased fluctuation in its density⁽³⁷⁾ when the temperature and pressure approach the critical point. Near the critical point, this fluctuation can generate vapor bubbles in the superheated liquid. For vapor bubbles larger than a critical radius, bubble growth will occur; bubbles smaller than the critical radius will collapse.⁽³⁷⁾ Once bubbles of a critical radius have been generated in the superheated liquid, the volume undergoes a

rapid transition into a mixture of vapor and liquid droplets. During explosive boiling, rapid expansion of the high-pressure bubbles in the liquid leads to a violent ejection of the molten droplets from the sample. The shadowgraph images of liquid droplets ejected from the silicon surface (see Figure 1a–c) indicate that the onset of the explosive boiling is at an irradiance of approximately $2.2 \times 10^{10}\text{ W cm}^{-2}$.

2.3.2 Laser Pulse Width

Laser wavelength and pulse duration also influence the quantity of ablated mass; the shorter the wavelength and pulse duration, the better the mass removal efficiency.^(15,16,23–26,28–30,38,39) Using an Nd:YAG laser with a 3-ns pulse duration, the ICPAES intensity was found to be almost an order of magnitude greater for UV

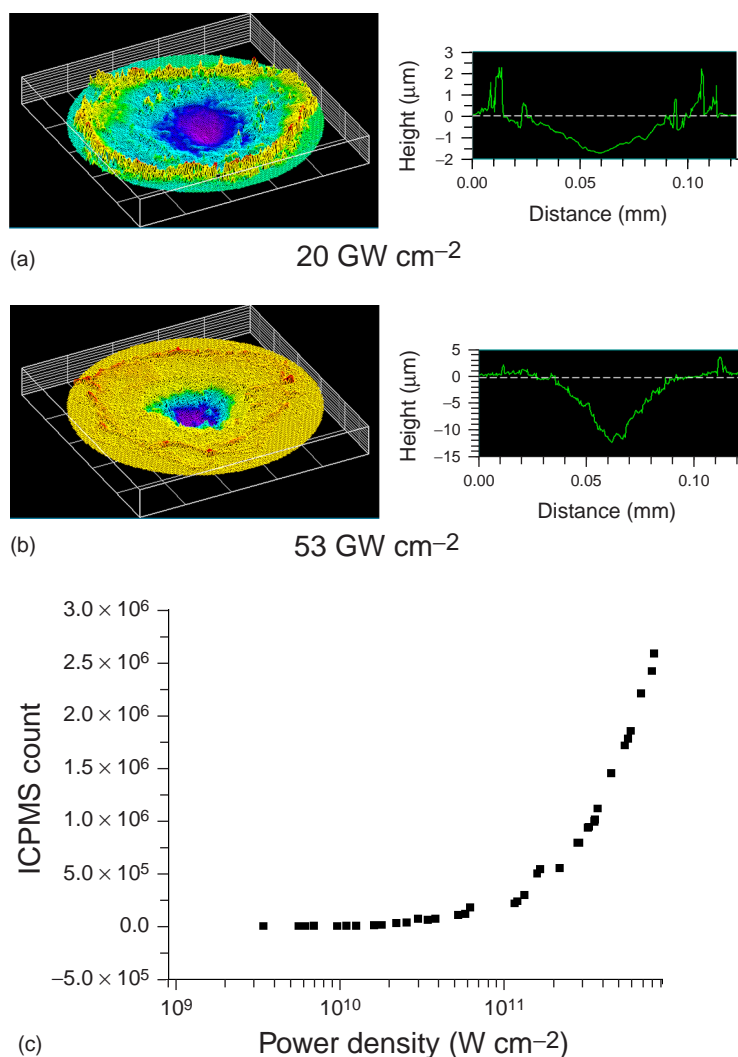


Figure 4 Crater profiles (a) before and (b) after an explosive boiling threshold. The crater depth changes dramatically from $1\text{ }\mu\text{m}$ to more than $10\text{ }\mu\text{m}$. (c) ICPMS signal versus laser power density. The ICPMS intensity increases dramatically across the threshold.

List of general abbreviations appears on back endpapers

than IR ablation sampling, with the same fluence. The absolute enhancement was found to be a function of laser irradiance.⁽³⁹⁾ When plasma shielding does exist, a lower wavelength is better because there is less absorption by the plasma; more energy is used to remove mass instead of heating the plasma. The shorter the laser pulse duration, the more efficient is the ablation process; picosecond laser pulses provided an order of magnitude greater signal intensity in ICPAES compared with a nanosecond pulsed laser with the same fluence. An explanation for increased mass ablation using picosecond pulses is that plasma shielding may be weaker; more laser energy is coupled to the sample than is absorbed by the plasma. Another possible mechanism is that more laser energy is converted to ablated mass instead of being lost in the sample through thermal dissipation, which is a function of pulse duration.⁽⁴⁰⁾ If the pulse duration is femtoseconds, the ablation process should be even more efficient.^(32,33) For femtosecond LA, the generation of vapor and a plasma will occur after the laser pulse is finished. Therefore, there should be no plasma shielding on the femtosecond timescale. Thermal diffusion to the solid also should be negligible. Currently, there are no reports of using femtosecond LA for chemical analysis. However, as femtosecond laser technology becomes more reliable, it is expected that new benefits to chemical analysis (and other applications) will be forthcoming.

2.3.3 Gas Environment

The gas atmosphere in the sample chamber can have a dramatic effect on ablation behavior.^(7,30,31,34,41,42) The use of different gases has been found to enhance sensitivity either by reducing plasma shielding or by influencing the ablated particle size distribution. With He in the ablation chamber, the mass ablation rate was 2–5 times and 10 times greater than that with Ar in the chamber for nanosecond and picosecond laser pulses, respectively.^(13,43) He and Ne provided an increased mass ablation efficiency compared with a decrease with Xe and Kr, relative to Ar for the nanosecond-pulsed LA. The enhancement or depression was found to be dependent on the laser irradiance. For picosecond LA sampling, only He provided an enhancement; there was very little influence on the mass ablation behavior by the other noble gases.

3 ANALYTICAL CHARACTERISTICS

A typical experimental system for LA sampling with the ICP is shown in Figure 5. In general, mass ablated from a target surface inside the sample chamber is entrained into an Ar gas flow and transferred into the ICP source,

where particles are first vaporized and then atomized and ionized. In most cases, the sample chamber is placed on a motorized or manually controlled micrometer translation stage. This is especially convenient for the analysis of heterogeneous samples, where different areas on a sample surface are to be analyzed. The individual components are described separately below.

3.1 Ablation Chamber and Transport Tubing

Various types of chambers have been described in the literature; a summary can be found in a review by Moenke-Blankenburg.⁽⁴⁴⁾ Typically, the sample is placed inside a chamber. However, there are cases in which the sample itself was the bottom of the chamber.⁽⁴⁵⁾ The simplest chamber can be a glass tube with two ports for gas flow, and a quartz window (or other transparent material at the laser wavelength) for laser beam delivery. Argon gas flow dynamics inside the chamber play a significant role in particle entrainment. With laminar flow in the chamber, entrainment efficiency and thus detection characteristics are improved; turbulent flow contributes to losses by trapping particles in stagnant flow regions.⁽⁴⁶⁾ The volume of the chamber is an important parameter; a larger internal volume can lead to sample dilution and memory effects. Because LA processes are transient in nature, larger chamber volumes may be advantageous for signal averaging during repetitive sampling experiments. Another important parameter is chamber length; if the laser beam window is located too close to the sample surface, vapor deposition can occur, reducing transmission and therefore the laser energy. Another issue concerning the chamber length is that different times are required for particles of different sizes to be entrained by the flow; larger particles will travel further before becoming entrained.⁽⁴⁷⁾ Depending on the flow velocity inside the chamber, large particles can be lost owing to collisions with the walls before entrainment.

Dispersion of different-sized particles in the ablation chamber depends on the Ar gas flow velocity in the chamber and can contribute to broadening of signal peaks (recorded during single laser pulse experiments). Further dispersion of ablated particles in the transport tube can occur and depends on the transfer tube length and internal diameter. To minimize dispersion, a short, narrow tube should be used. Although particle dispersion in the chamber and transport tube may be important for analysis during single laser pulse experiments, there are no significant advantages to using a short tube during LA sampling with repetitive pulses.

3.1.1 Mass Transport Efficiency

For a given ablation chamber/tube configuration, particle transport efficiency depends on the ablated particle

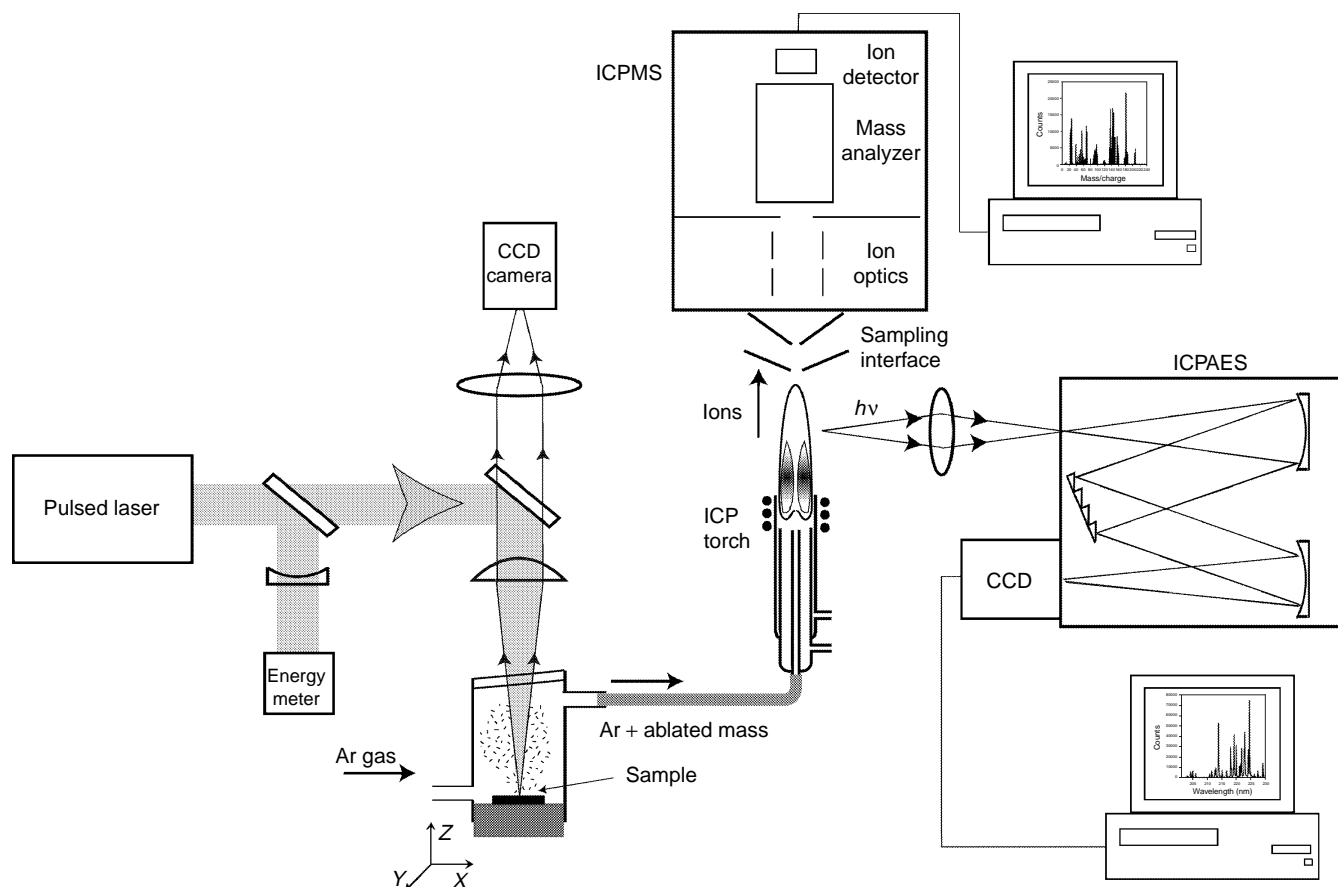


Figure 5 Schematic diagram of LA sampling into an ICP source. CCD, charge-coupled device.

size distribution. The number of particles and their size distribution depends on the laser and sample properties.^(22,47,48) The volume distribution of laser-generated particles changes with respect to the laser wavelength; there are more large particles generated with an IR laser than with a UV laser.⁽⁴⁸⁾ Since melting and melt-fusing may be responsible for the generation of particles, a thicker molten layer may produce a greater fraction of large particles. The optical absorption depth in most solid samples is greater for IR than UV wavelengths. Therefore, a larger molten liquid volume may be responsible for large particle production using IR LA.

Entrainment of ablated mass into the gas stream and transport to the ICP are particle size dependent. Large particles may not be entrained and those that are may not completely vaporize in the ICP. Particle sizes should be less than about $2\mu\text{m}$ for efficient transport to and excitation in the ICP.^(45,49,50) Particle entrainment efficiency can be defined as the ratio of mass entering the ICP to the total mass ablated from the sample. Particle entrainment efficiency has been found to decrease with increasing laser irradiance. Entrainment efficiency was about 25% at low irradiance and decreased to about

5% at high irradiance.⁽⁴⁷⁾ One possible reason for the small entrainment efficiency at high irradiance may be the formation of excessively large particles ($>5\mu\text{m}$); large particle ejection is observed in Figure 1(a–c). The removal of large fractured pieces ($>\sim 50\mu\text{m}$), possibly due to increased thermal stress and pressure on the sample surface, was also observed after ablation at high irradiances (Figure 6). These very large particles will not be entrained into the argon gas flow, but instead will settle in the ablation chamber due to gravity. Transport efficiency as a function of particle-size distribution needs to be critically studied for improving LA sampling in atomic spectroscopy.^(45,51) A few studies have addressed particle transport, with preliminary data suggesting that particles in the $0.1\text{--}1.0\mu\text{m}$ range reach and vaporize in the ICP.^(22,45,48)

Literature values for LA transport efficiency are in the range of about 5–40%.^(45,47) The large variation represents the effects of laser beam conditions, sample material properties, and ablation chamber/transfer tube geometries. In general, particle losses in the sample chamber and transport tube are mainly due to gravitational settling or inertial impact to the walls for large

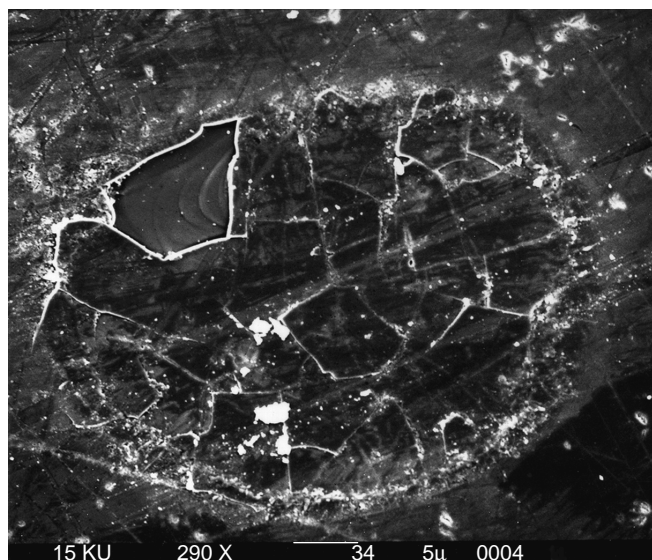


Figure 6 Scanning electron microscope image of an ablated glass surface. A large piece ($\sim 50\mu\text{m}$) of the cracked sample was removed from the ablation spot.

particles, and diffusion to the walls for smaller particles. These processes depend on the tube length and internal diameter. Transport efficiency for larger particles, which represent most of the ablated mass and thus are responsible for most of the ICP signal, can be improved by utilization of a short, narrow tube. Generally, particles in the range $0.1\text{--}1.0\mu\text{m}$ are most efficiently transported to the ICP. For a given tubing length and diameter, theoretical calculations predict losses to be flow dependent. In practice, however, no significant differences in the ICPMS signal count rates were observed when the Ar flow rate was varied from 0.1 to 0.9 L min^{-1} during ablation of Zr metal. Particle losses inside the sample chamber and transport tube can contribute to memory effects. To minimize these effects, it is recommended that the transport tube be cleaned regularly or replaced, and the system flushed with Ar gas at increased flow rates between measurements.

3.2 Laser Systems and Optics

Over the years, several pulsed lasers have been tested for ablation. Ruby (694.3 nm), CO_2 ($10.6\mu\text{m}$), free-running Nd:YAG and excimer lasers have been shown to efficiently ablate solid samples.⁽¹⁾ However, Q-switched Nd:YAG lasers with nanosecond pulses have become the most prevalent systems used for LA today. These lasers are relatively inexpensive, easy to operate, and compact, have good pulse-to-pulse and long-term stability characteristics, and deliver sufficient energy for ablation. The fundamental harmonic of 1064 nm can be easily doubled (532 nm), tripled (355 nm), quadrupled (266 nm),

and quintupled (213 nm). The Q-switched Nd:YAG laser operated at the fourth harmonic is currently the most popular for LA chemical analysis. Recently, it has been shown that samples with relatively low absorption at 266 nm , such as calcite and garnet, can be more efficiently ablated with the Nd:YAG at 213 nm ⁽⁵²⁾ or the ArF excimer (193 nm).⁽⁵³⁾

The laser beam is transferred to the sample chamber by means of mirrors, beam splitters, and/or prisms. In the simplest system, focusing is achieved with a plano-concave singlet lens, which has a low degree of spherical aberration. Laser beam spot size at a sample surface can be easily adjusted by translating the lens relative to the sample. The minimum spot size with radius, w , that can be achieved by focusing a Gaussian diffraction-limited laser beam can be approximated by Equation (1):

$$w \propto \frac{\lambda f}{\pi w_0} \quad (1)$$

where λ is the laser wavelength, f is the lens focal distance, and w_0 is the initial laser beam radius. By using a lens with a short focal distance and a wide initial beam diameter, the smallest LA spots (best spatial resolution) can be achieved. An optical microscope equipped with a CCD camera is an excellent addition to experimental systems, allowing easy focusing of the laser beam on to a selected sample location, with beam spot sizes in the order of several micrometers. Such systems are widely used, especially for the analysis of geological samples where a high degree of spatial resolution is required.

3.3 Inductively Coupled Plasma Atomic Emission Spectroscopy and Inductively Coupled Plasma Mass Spectrometry Instrumentation

In contrast to liquid nebulization sample introduction, LA sampling is transient in nature. Thus, simultaneous detection of elements is needed. Single-channel instruments equipped with a photomultiplier tube (PMT) require scanning of a monochromator grating. Such systems are not very useful for transient signal detection when detection of more than one element is required. Direct-read polychromators can employ more than 60 exit slits with PMTs for detection of numerous wavelengths, providing simultaneous multielement capability. The photodiode array (PDA) and more recently the charge transfer device (CTD) used with a conventional Czerny–Turner-type spectrometer can cover spectral windows of several tens of nanometers simultaneously. Spectrometers with Paschen–Runge polychromators and with échelle gratings, equipped with solid-state detectors, have multielement capability and provide simultaneous UV and visible spectral coverage.

Most commercially available ICPMS instruments utilize radiofrequency quadrupole mass analyzers. Although quadrupole mass analyzers typically have a low resolution capability (c. 0.5 u), their low cost, ease of coupling with an ICP source, and pseudosimultaneous mass detection make them attractive for elemental analysis with LA applications. The complete mass range from 1 to 250 u can be scanned in about 0.1 s.

Many LA applications require high-precision isotopic ratio measurements; high-resolution double-focusing ICPMS instruments equipped with multicollector array detectors are well suited for this purpose. ICPMS instruments with time-of-flight (TOF) analyzers were recently demonstrated with LA sampling.⁽⁵⁴⁾ The TOF approach allows the collection of several thousand complete mass spectra per second. Owing to the transient nature of LA, ICPMS with a TOF analyzer is potentially advantageous for multielemental determinations, although to date only limited research has been conducted.

The detection capabilities of LA with ICPAES and ICPMS techniques depend significantly on the experimental conditions and equipment. ICPMS is typically used for minor and trace elemental analysis, whereas ICPAES has lower sensitivity and is primarily used for the analysis of major and minor constituents. Most geological applications, which require a high degree of spatial resolution for accurate microanalysis of inclusions and grains in minerals, utilize ICPMS instrumentation.

3.4 Detection Limits

One of the advantages of dry ICP conditions from LA sample introduction is that plasma excitation/ionization temperatures and electron number densities are typically higher than with a wet plasma produced during liquid nebulization. Dry plasma conditions enhance ionization and excitation processes. This benefit, along with simplified mass spectra (due to reduction of polyatomic interferences), provides improved detection characteristics. Absolute detection limits (absolute detectable amount of analyte mass) for rare-earth elements in silicate samples were shown to be two orders of magnitude better for LA ICPMS than liquid nebulization sample introduction.⁽⁵⁵⁾ However when relative detection limits (detectable analyte concentration in a sample) are compared, liquid nebulization sample introduction is better. This situation only exists because the amount of mass nebulized into the ICP is much greater than that ablated by the laser. Assuming a 2% efficiency for conventional pneumatic nebulizers with a 1 mL min⁻¹ sampling rate, roughly 20 mg min⁻¹ of solution is introduced into the ICP. In contrast, the amount of ablated mass per laser pulse is typically only 1 ng–1 µg. Hence for a laser repetition rate of 10 Hz and a particle transfer efficiency of 40%

(maximum value reported in the literature), the amount of mass introduced into the ICP is only from 0.2 µg min⁻¹ to 0.2 mg min⁻¹. Hence the mass per unit time introduced into the ICP as a result of LA is about 10²–10⁵ times less than that from liquid nebulization. Relative detection limits depend on the amount of mass and are therefore better for liquid nebulization sample introduction.

Typical detection limits, determined as three times the standard deviation of the blank, are in the low micrograms per gram and even nanograms per gram range for ICPMS detection with LA, in contrast to the picograms per gram level for liquid nebulization. For LA sampling with ICPAES, laser energies of 10–100 mJ are required, compared with only few milli- or even microjoules for sampling into the ICPMS. Typical LODs for LA sampling with ICPAES are in the micrograms per gram range and are comparable to those available from liquid nebulization sampling with ICPAES. Better detection limits can be achieved by increasing the amount of ablated mass per laser pulse, which can be realized by improvement in the laser energy coupling efficiency to the sample and/or improvement in entrainment/transport efficiency. When a sample was ablated inside the ICP torch, just below the discharge, particle losses associated with mass entrainment and transport were eliminated, and a significant improvement in detection characteristics was achieved.⁽⁵⁶⁾

3.5 Calibration and Optimization

The signal intensity recorded by ICPAES and ICPMS during sample introduction (both liquid nebulization and solid sampling) is proportional to the concentration of an element of interest in the sample. Absolute measurements require calibration procedures to be established, which remains an essential issue for chemical analysis.^(1,5,44,57) For liquid sample introduction, standards are relatively easy to obtain in the form of single- or multielemental solutions; linear calibration curves can be generated over three to six orders of magnitude for ICPAES and eight orders of magnitude for ICPMS.⁽⁵⁷⁾ Assuming similar viscosities for the diluted sample and the standard solutions, the amount of aerosol aspirated into the ICP is determined by the nebulizer/spray chamber parameters. In contrast, during LA the amount of mass ablated and transported into the ICP may be different for samples and standards, if the standards are not matrix matched. For LA, an internal or external standardization procedure is required to compensate for changes in the quantity of mass ablated, even when the analyte concentration remains constant. Matrix-matched solid standards are generally required for instrument calibration.

3.5.1 Internal Standardization and Matrix Matching

The ablated mass is determined by the properties of the matrix, and close matching of calibration standards to samples is preferred. However, the chemical form in which the analyte is present in the sample was shown to influence the elemental response.⁽⁵⁸⁾ Compensation for this effect often can be performed by normalization of analyte intensity to that of another element (internal standard). This procedure requires that the concentration of the internal standard, usually the matrix element, be either known [determined from independent methods, such as X-ray fluorescence (XRF) spectroscopy] or be constant in the sample and standards. In most cases, an internal standard provides excellent compensation for differences in ablation behavior for samples and standards. For trace elements in homogeneous samples, this approach has been used to improve the measurement precision to better than 1%.^(18,49,59) Internal standardization is especially useful for bulk analysis with samples and standards pressed into pellets,⁽⁶⁰⁾ fused into glass beads,⁽⁴⁹⁾ or preconcentrated in an NiS button⁽⁶¹⁾ where the internal standard is added during sample preparation. A single calibration graph was used for analysis of silicate rocks and limestones fused with Sc and Y oxides as internal standards.⁽⁶²⁾ For cases in which relatively “good” standards were available, LA proved to be a reliable and accurate chemical analysis procedure. In some cases, however, internal standardization can be limited by differences in the ablation behavior of the sample and the standards, especially when standards are not matrix matched. For example, elemental fractionation of W relative to the internal standard Ca was shown to be different for a scheelite sample and a silicate glass calibration standard.⁽⁶³⁾

Calibration without an internal standard has been shown to be possible, especially in cases where only trace level impurities differ among the standards and sample; the trace impurities do not effect ablation behavior. Linear calibration curves were established and accurate trace elemental analysis was demonstrated for U,⁽⁶⁴⁾ Au and Ag,⁽⁶⁵⁾ and glass⁽⁶⁶⁾ without internal standardization. In contrast, if the matrix properties change because of changes in the analyte concentration, the LA behavior is affected. For example, for the analysis of Zn in brasses, where Zn is a major element, linear calibration cannot be achieved, and other signal normalization procedures are needed for accurate calibration.⁽⁶⁷⁾

When internal standardization procedures are used for analyte characterization in an unknown sample, Equation (2) is applied:

$$C_{sa}^M = C_{sa}^{IS} \frac{I_{sa}^M C_{st}^M I_{st}^{IS}}{I_{sa}^{IS} C_{st}^{IS} I_{st}^M} \quad (2)$$

where C is the concentration and I is the ICP signal intensity. Subscripts sa and st denote sample and standard and superscripts M and IS correspond to the unknown analyte and the internal standard, respectively. This relationship assumes that the concentration of the internal standard is known and that fractionation between the analyte and internal standard is not significant, or is the same for analyte and standards.

3.5.2 Calibration with Liquid Standards

For many samples, matrix-matched standards will not be available. In these cases, external calibration can be performed using nebulization of liquid standards; a dual sample introduction method can be used to establish instrumental calibration with a series of standard solutions. To analyze the unknown sample by LA using liquid standards, wet ICP plasma conditions must be maintained.⁽⁶⁸⁾ However, the use of liquids for calibration defeats two important advantages of LA and dry ICP: elimination of isobaric interferences in ICPMS and the generation of solvent waste.⁽¹²⁾ In addition, optimum ICP conditions will not be the same for LA and solution nebulization. For nebulization, the analyte dries from liquid droplets to form small particles in the plasma. For LA sampling, larger dry particles are introduced directly into the ICP.^(45,48) Atomization and excitation processes in the ICP are expected to be different for these two cases. Even if the water content is the same in the ICP, it is still possible that the excitation characteristics will be different because of the different vaporization mechanisms for nebulized solution and laser-ablated particles. On the other hand, calibration with dried solution aerosol⁽⁶⁹⁾ or by direct LA of liquids^(70,71) does not significantly perturb dry ICP conditions.

LA of liquids has been shown to be effective for the analysis of microscopic fluid inclusions in minerals. In this method, direct ablation of a standard solution was used for external ICPMS calibration with Na as an internal standard.⁽⁷¹⁾ In another study, instrument calibration was done by using artificial fluid inclusions prepared by drawing a standard solution into a microcapillary tube⁽⁷²⁾ or with microwells containing aqueous solutions.⁽⁷³⁾

3.5.3 External Standardization

For some samples, internal standardization may not be a viable option. In such cases, external standardization must be used to compensate for differences in ablation of the sample versus the standards. Several external procedures have been demonstrated to compensate for changes in the quantity of ablated mass. They include light scattering,^(48,74,75) acoustic emission in the sample^(19,76,77) or in the ambient medium,^(76,78) the use of a mass monitor

to collect a portion of the laser-ablated aerosol,⁽⁷⁹⁾ and the measurement of spectral emission intensity in the ICP and laser-induced plasma simultaneously.^(34,77) An absolute method to quantify the amount of mass ablated is to weigh the sample before and after ablation.⁽⁸⁰⁾ However, such direct mass measurements are tedious and may not be accurate because of the small quantity (<1 µg) of mass ablated for each laser pulse, and because transport efficiency is not included.^(22,45) Determination of mass ablation and transport efficiencies is possible by collecting particles on a nonporous filter, which is an indication of the total mass transported to the ICP.

4 APPLICATIONS

Because of the unique properties of the laser, many novel applications for chemical analysis using the ICP have been demonstrated. This section presents a brief overview of applications that would be difficult or impossible to perform without the use of LA. Most of the applications utilize ICPMS because of its enhanced sensitivity.

4.1 Environmental and Oceanography

4.1.1 Tree Rings

Spatial patterns in the chemical content of tree rings can be used as a monitor for changes in atmospheric conditions, changes in soil chemistry, and the pollution history of an area. Laser ablation inductively coupled plasma mass spectrometry (LA/ICPMS) is an excellent approach to determine chemical content in tree samples because of the high spatial resolution provided by the focused laser beam, and the excellent sensitivity of ICPMS to measure very low detection levels for many elements.^(81–84) Watmough et al.⁽⁸³⁾ obtained the quantitative multielement analysis of 11 elements in red maple tree rings; significant changes in these elements were measured for trees grown in contaminated soils adjacent to a metal smelter versus trees grown in unpolluted soils. GarbeSchongberg et al.⁽⁸⁴⁾ analyzed pine and birch tree rings from Norway and Russia and discussed the elemental relationship with the pollution history of these areas.

4.1.2 Sea Shells

Trace-element fluctuations in sea shells represent environmental changes and major pollution events. In the work of Raith et al.,⁽⁸⁵⁾ the inner to the outer walls of a shell were analyzed; the elemental changes between growth bands of the shell showed a history of heavy-metal pollution over the years. Vander Putten et al.⁽⁸⁶⁾

measured spatial variations of Mg, Mn, Sr, Ba, and Pb in the calcite layer of *Mytilus edulis* sea shells.

4.1.3 Airborne Particulates

The analysis of trace elements in airborne particulates provides unique signature information for monitoring air quality and air pollution. For example, arsenic, considered the major “marker element” of air pollution, is one of the most hazardous anthropogenic air pollutants affecting humans globally. Traditionally, membrane filters with small pore size have been used for collecting particulate samples. The entire filter is then digested and the total volume analyzed. LA is a perfect alternative for such analyses; the particulates can be ablated directly from the filter media. Tanaka et al.⁽⁸⁷⁾ and Wang et al.^(88–90) analyzed airborne particulates for more than 20 major, minor, and trace elements using this approach.

4.1.4 High-resolution Analysis of Coral

The concentration of trace elements in coral skeletons can provide information about changes in seawater properties; calcification in reef-building corals is strongly affected by environmental factors such as temperature, light, water motion, and pollution.⁽⁹¹⁾ As coral grows, it secretes a calcareous skeleton into which trace elements are partitioned from the ambient seawater. Spatial analysis of the coral skeleton allows a detailed investigation of seasonal composition changes.^(92,93) Compared with the traditional method of sample milling, with processing and analysis by solution nebulization, LA/ICPMS provides in situ analysis of corals with spatial resolution less than 20 µm. Sinclair et al.⁽⁹²⁾ analyzed corals collected from Australia and showed that the elements B, Mg, Sr, and U exhibited seasonal variations, as shown in Figure 7. These fluctuations coincided with the changes of sea-surface temperature.

4.2 Geochemistry and Cosmochemistry

4.2.1 Uranium–Lead Geochronology

Zircon U–Pb geochronology is one of the principal dating tools used in the earth sciences; ages are calculated by measuring ²⁰⁶Pb/²³⁸U, ²⁰⁷Pb/²³⁵U, and ²⁰⁷Pb/²⁰⁶Pb ratios. The conventional method for U–Pb isotopic analysis has been by thermal ionization mass spectrometry (TIMS) with chemical separation. However, very low blank values are required and the data represent the “average” of the bulk grains. LA/ICPMS has the ability to perform spatially resolved in situ analysis of U–Pb isotopic compositions in zircons and similar minerals. Several groups^(94–97) have studied zircon and monazite samples using LA/ICPMS. Most of these studies only

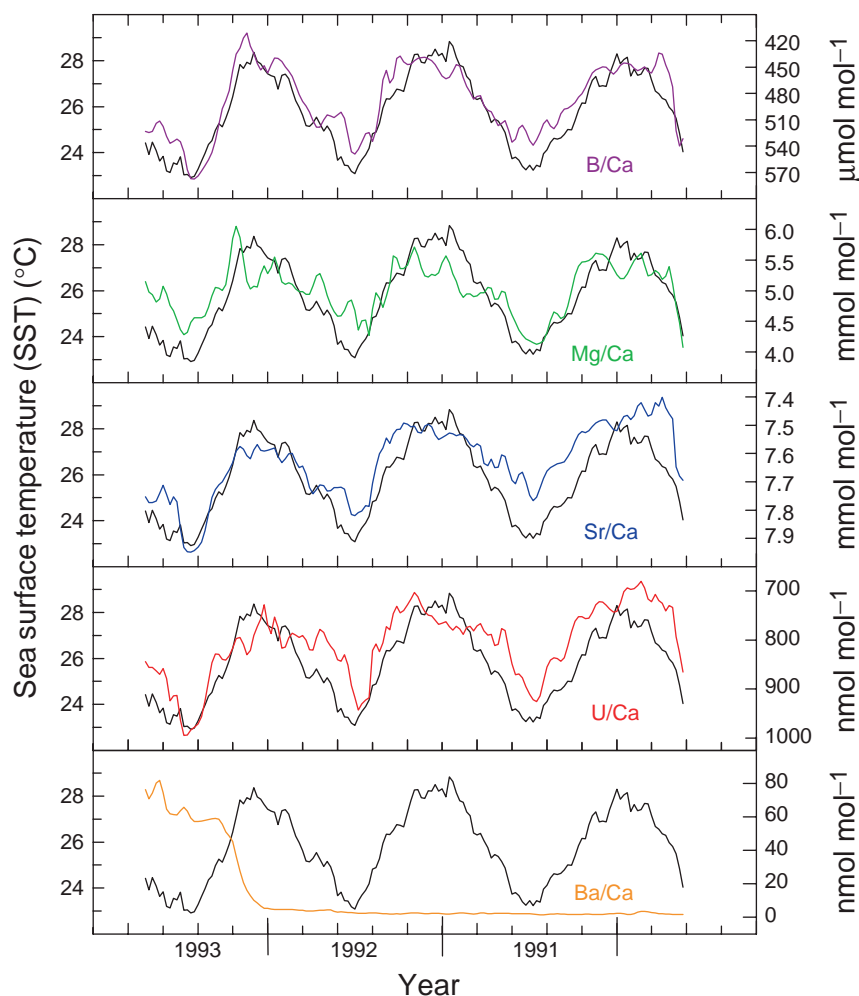


Figure 7 Trace element and sea surface temperature (SST) profiles for coral from Australia's Great Barrier Reef. Colored lines represent an average of three trace element profiles taken over the same coral track. Black lines are the instrumental SST data taken from the weather station. B, Mg, Sr, and U all display clear seasonal variation. Ba does not show a seasonality but displays a marked enrichment in the tissue zone. (Figure reproduced from original data with permission by Dr Daniel J. Sinclair⁽⁹²⁾.)

show $^{207}\text{Pb}/^{206}\text{Pb}$ data and a few include the $^{206}\text{Pb}/^{238}\text{U}$ ratio, because of a fractionation problem. Without the $^{206}\text{Pb}/^{238}\text{U}$ ratio, the analysis cannot be extended to "young" (<600 Ma) zircon dating. In order to minimize Pb–U fractionation, methods such as active focusing, line scanning, and soft ablation (increasing the laser power when ablation is progressing) were attempted. Solving Pb–U fractionation is necessary to the success of LA/ICPMS for this application.

4.2.2 Inclusion Analysis

Microscopic inclusions in minerals contain direct evidence of the composition of fluids associated with large-scale material transport in the Earth's interior. Quantitative knowledge of the elements and isotopic composition of these fluid inclusions is a prerequisite for understanding

and modeling fluid–rock interactions. Detailed chemical information is difficult to obtain because of the very small size of these inclusions (typically 10^{-11} – 10^{-9} g).⁽⁷⁰⁾ Crush–leach analysis or bulk analysis of quartz containing fluid inclusions can provide concentration ratios averaged over many inclusions, but most samples contain multiple generations of fluid inclusions of different compositions. LA/ICPMS for the analysis of individual microscopic inclusion has, therefore, received considerable attention. Good quantitative results have been published mainly for synthetic fluid inclusions,^(73,98) where a heavy trace element of a known concentration (e.g. Sr, U) was added as an internal standard. Günther et al.⁽⁷⁰⁾ reported a method for measuring complex polyphase inclusions using a step-wise opening procedure. A series of inclusions representing the fluid before, during, and after the deposition of cassiterite (SnO_2) in a tin deposit in Australia were analyzed

by this method; physical and chemical mechanisms of ore precipitation were proposed based on these data.⁽⁹⁹⁾

4.2.3 *Precise In Situ Analysis of Hafnium, Tungsten, Strontium, Lead, and Osmium Isotopes*

Many elements are of significant interest for isotope geochemistry and need to be measured at trace levels with excellent precision. Multiple collector inductively coupled plasma mass spectrometry (MC/ICPMS) with a magnetic sector is a new technology for the measurement of isotopic compositions with very high precision. It is particularly suited for elements with high first ionization potentials such as Hf, W, and Os, which cannot be measured with good precision using conventional TIMS. Combined with LA sampling, in situ isotopic measurements at the microscopic scale are possible. Although this technology is still in its infancy, diverse applications have already led to a number of important scientific developments.⁽¹⁰⁰⁾

The initial Hf isotopic composition is more reliable than initial Nd as a geochemical tracer owing to the immobility of Hf. The Hf isotopic composition in zircon samples was analyzed by Thirlwall and Walder.⁽¹⁰¹⁾ In low-temperature geochemistry, Hf isotopes may provide the most reliable and sensitive isotopic proxy for hydrothermal activity in the ocean. The Hf isotopic compositions in iron–manganese nodules and crusts were studied by Godfrey et al.⁽¹⁰²⁾ and the data reflected the concomitant growth from seawater and pore fluids. There is strong interest in measuring W and Hf isotopic compositions with high precision using LA with MC/ICPMS. The ¹⁸²Hf–¹⁸²W system is a method for constraining timescales of accretion and metal–silicate differentiation in planets; the age of the Earth's core, the moon, and Mars have been measured using this new chronometer.⁽¹⁰⁰⁾

Sr and Pb isotopic compositions are significant for geochemistry and oceanography research. Analysis of these elements traditionally requires complicated chemical separation procedures. LA with MC/ICPMS provided accurate and precise measurement of ⁸⁷Sr/⁸⁶Sr isotopic ratios in geological materials.⁽¹⁰³⁾ Pb isotopic compositions in a ferromanganese crust from the Pacific ocean were analyzed by Christensen et al.⁽¹⁰⁴⁾ and the authors concluded that the Pb isotopic data could be used to probe climate-driven changes in ocean circulation. Analysis of Os isotopic ratios for iridosmine samples was reported using LA with MC/ICPMS.⁽¹⁰⁵⁾ The mineral iridosmine has been used for the definition of the Os isotopic evolution of the mantle.

4.2.4 *Bulk and Microbeam Analysis of Rocks and Minerals*

Bulk and spatial analyses of rocks and minerals for

elemental and isotopic compositions can provide fundamental information to help solve diverse geological and environmental problems. The application of LA/ICPMS for the analysis of whole-rock geological samples, such as pressed power pellets and lithium metaborate fusions, has been described by several authors.^(106,107) In most of these studies, the measurement of rare-earth elements (Zr, Hf, U, Th, Sr, Rb, Ba, Nb, Ta) was emphasized. LA/ICPMS was also used to determine the platinum group elements (Ru, Rh, Pd, Os, Ir and Pt) and gold, which have very low natural abundance but great economic and geological importance.⁽¹⁰⁸⁾

The spatially resolved analysis of elements within minerals provides crystal-growth information and the variation in the physical and chemical nature of environments in which they grew. LA/ICPMS analysis, either on a single mineral grain or on a thin section, can provide such information. LA/ICPMS analyses of minerals such as calcite, zircon, olivine, plagioclase, feldspar, titanite, apatite, clinopyroxene, amphibole, and garnet have been reported.^(109–111)

4.3 Forensics and Authentication

4.3.1 *Authentication of Antique Objects*

Chemical analysis is an excellent approach for verifying the authenticity of valuable artifacts. Obviously, the analytical method for authenticity verification of precious antiques should be either nondestructive or require extremely small sample quantities. Using LA/ICPMS, visible damage can be restricted to an acceptable minimum. Such studies were reported by Devos et al.,⁽¹¹²⁾ in which a specially designed sample chamber was used, and almost invisible 100-μm craters were produced on antique silver objects. The elements Zn, Cd, Sn, Sb, Au, Pb, and Bi were measured, and their contents were used to distinguish forgery in silver antiques. Similar studies were reported by Wanner et al.⁽¹¹³⁾ for trace element analyses of archaeological samples such as ancient coins, various antique silver items, and ancient iron. Owing to surface roughness of the samples, an autofocus system was used to achieve reproducible ablation conditions. In these experiments, a lateral resolution of 50 μm and absolute detection limits of 1–1.4 pg were achieved.

4.3.2 *Fingerprinting Crime Scene Evidence*

Many criminal activities result in the generation of debris or other materials, which become available to investigating authorities as physical evidence of the crime. However, the generation of traditional analytical and forensic chemical data is often costly and time-consuming. LA/ICPMS offers the potential for producing fast, definitive, and cost-effective forensic chemical analysis for

use in identifying physical evidence that relates a suspect to the scene of a crime. Watling et al.⁽¹¹⁴⁾ examined several kinds of glass and steel samples as physical evidence of a crime. They developed software to facilitate an intercomparison of three elements simultaneously (ternary plots) for large groups of samples. This approach established both the reproducibility of the “fingerprint” and the uniqueness of interelement associations. A similar idea was used to source the provenance of cannabis. Certain elements from a specific area or geological environment characterize uniquely the source of the plant. Watling⁽¹¹⁵⁾ showed the trace element association “fingerprint” patterns of cannabis crops and the potential tracing of these crops to specific geological environments. The association of elements formed the basis for determining the provenance of cannabis crops and samples recovered during police drug raids.

4.4 Waste-sample Analysis

LA has many advantages when used to analyze radiological contaminated samples. For example, organic solvents or concentrated acids that are required for classical separation procedures will not be needed for LA sampling. Also, with LA, much less total sample ($<1\ \mu\text{g}$) will be required, greatly reducing the risks associated with sample handling and contamination, and personnel exposure. Finally, elemental and isotopic analysis can be obtained entirely within a hot cell environment, further reducing the risk of contamination.⁽¹¹⁶⁾ High-level waste analysis using LA/ICPMS was detailed by Smith et al.⁽¹¹⁷⁾ A unique LA facility has been established in a hot cell environment at the Hanford Site for direct characterization of tank waste samples. Applications of LA and high-resolution ICPAES in the nuclear industry,

especially high-resolution isotopic analysis of U and determination of lanthanides, were reported by Giglio et al.⁽¹¹⁶⁾ and Zamzow et al.⁽¹¹⁸⁾

5 NON-INDUCTIVELY COUPLED PLASMA APPLICATIONS

There are many LA applications that do not rely on particle digestion by an analytical source (ICP, flame, etc.), but instead directly measure the ablated atomic mass. Laser-induced breakdown spectroscopy (LIBS), described in more detail in the article **Laser-induced Breakdown Spectroscopy**, involves monitoring spectroscopic emission intensity directly in the laser plume. Other applications involve direct MS detection of the ablated mass, with and without secondary ionization, e.g. resonance ionization mass spectrometry (RIMS) and matrix-assisted laser desorption/ionization (MALDI). It would be impossible to discuss these numerous applications without doubling the length of this article. Instead, one particular technique employed by our research group is presented.

5.1 Laser Ablation Ion-storage Time-of-flight Mass Spectrometry

A new technique for single particle analysis was developed that uses ion-trap and TOF mass spectrometers. Commercial LA systems with imaging capabilities involve a chamber in which the ablated mass is entrained into a gas stream and transported to the analytical source by several meters of tubing, thereby diluting the mass vapor and influencing detection sensitivity. For single-particle analysis, excellent sensitivity must be available because of

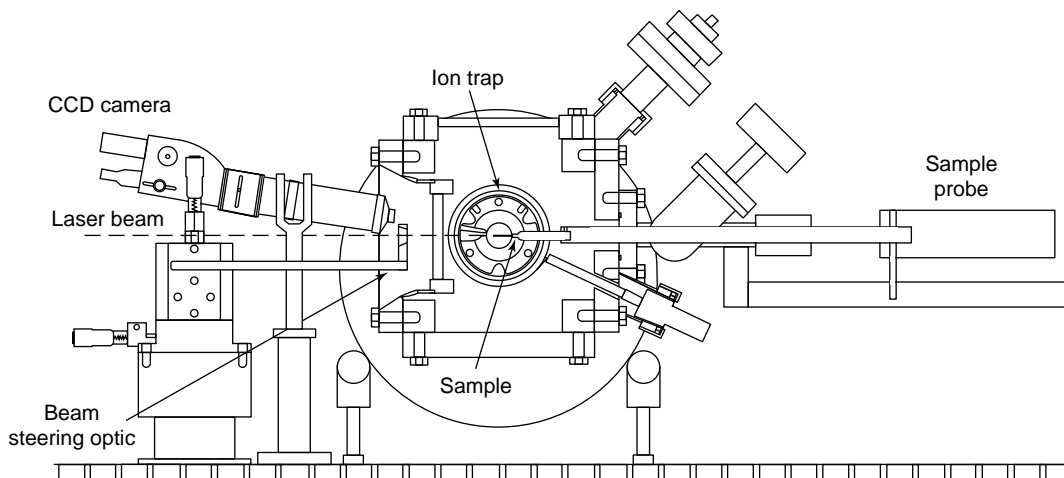


Figure 8 Schematic diagram of ion-trap TOF mass spectrometer with imaging capabilities. The system was designed such that a pulsed Nd:YAG laser beam could ablate a selected sample inside the ion trap mass spectrometer.

the limited absolute mass from a micrometer-sized particle. To overcome the dilution and sensitivity limitations, an instrument was developed using LA inside an ion-storage time-of-flight mass spectrometry (IS/TOFMS) system with an imaging camera to observe, select, vaporize, ionize, and analyze individual particles or spatial locations on a solid surface.

An ion trap was designed such that a pulsed Nd:YAG laser beam could ablate a sample affixed to a probe inserted radially through the ring electrode (Figure 8). Once the particle is selected using the imaging system, it is directly ablated/ionized by the laser beam. A primary advantage of this system is that the ions are generated directly inside the ion trap. The ion trap is not used as the mass spectrometer, because space-charge effects would critically influence the mass resolution. Instead, the ion trap is used only as a storage device and the TOF performs the MS. In this way, space charging is significantly reduced except in cases when using extremely high laser fluence, which is not necessary for excellent sensitivity. In preliminary experiments, trace contaminants of Ag,

Sn, and Sb were measured in a Pb target with a single laser shot. Reproducible spectra could be measured with only approximately 10 μ J of laser energy. The laser-beam focusing system provided a spatial resolution of approximately 12 μ m, with imaging capability to guide the laser beam to a specific location on the sample. The photographs in Figure 9(a) and (b) show images of the laser-induced craters in hair and alloy samples, respectively.

6 PERSPECTIVES AND FUTURE TRENDS

LA and atomic spectroscopy have become a mature partnership providing significant benefits to both techniques. On the one hand, LA provides the best method for directly converting a solid-phase sample into gas-phase constituents. On the other hand, atomic spectroscopy brings to the relationship a powerful method for understanding the fundamental mechanisms of ablation processes. For atomic spectroscopy, the relationship is continuing to flourish, as can be seen by the increasing number of applications, number of published papers and conference symposia, and new commercial systems. This article has primarily addressed LA as a sampling technique for atomic spectroscopy. There are numerous papers in the literature in which atomic spectroscopy is used to study the fundamental behavior of ablation processes; an example is the work by Bushaw and Alexander using high-resolution time-resolved atomic absorption spectroscopy for the investigation of LA plume dynamics.⁽¹¹⁹⁾ A literature search using the two keywords "laser" and "ablation" provided approximately 2500 published papers in the *Current Contents* database, increasing continuously from 1990 to the present. Interest in LA continues to flourish because of applications in atomic spectroscopy, and also medical, semiconductor, materials, and other areas. When matrix-matched standards are available, LA is an ideal quantitative method with excellent accuracy and precision. In cases when matrix-matched standards are not available, LA with atomic spectroscopy is suitable for semiquantitative analysis. Further development of LA and its maturation into an accurate and precise sampling technique for atomic spectroscopy will occur through understanding of fundamental processes and the means to control them. The benefits of LA sampling and atomic spectroscopy warrant success.

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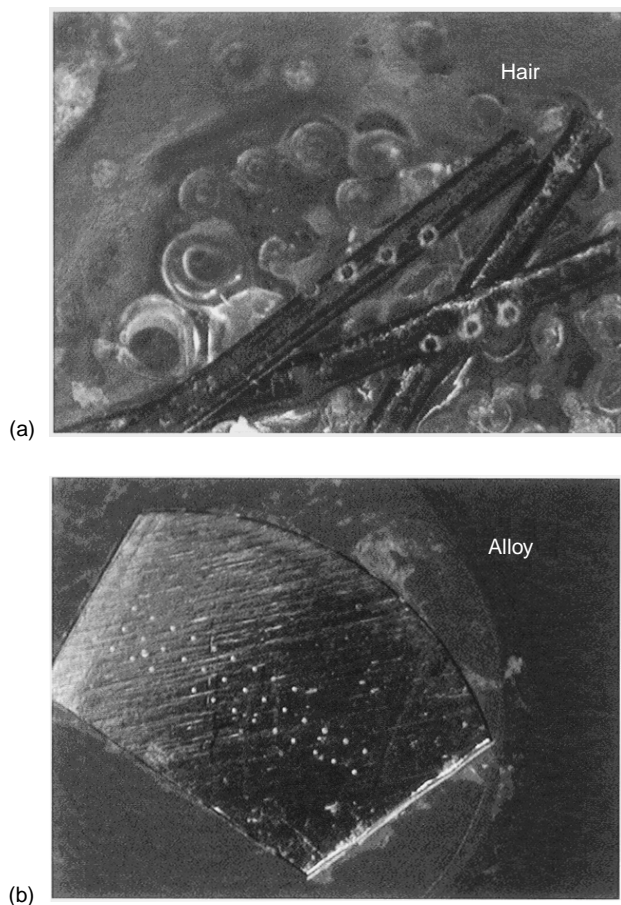


Figure 9 Images of the laser-induced craters in (a) hair and (b) alloy samples.

List of general abbreviations appears on back endpapers

researchers whose papers are referenced in this work, with special thanks to Sungho Jeong, Sam Mao, George Chan, and Jong Yoo for contributing data. R.E.R. also acknowledges G.L. Klunder, P.G. Grant, and B.D. Andresen for the work on IS/TOFMS at Lawrence Livermore National Laboratory (LLNL). This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, and by the Environmental Waste Management Science Program (EMSP) under a joint grant from the Office of Energy Research and Office of Environmental Management, through the LBNL under Contract No. DE-AC03-76SF00098.

ABBREVIATIONS AND ACRONYMS

AES	Atomic Emission Spectroscopy
CCD	Charge-coupled Device
CTD	Charge Transfer Device
DCP	Direct Current Plasma
DSI	Direct Sample Insertion
EMSP	Environmental Waste Management Science Program
ETV	Electrothermal Vaporization
GD	Glow Discharge
ICP	Inductively Coupled Plasma
ICPAES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IR	Infrared
IS/TOFMS	Ion-storage Time-of-flight Mass Spectrometry
LA	Laser Ablation
LA/ICP	Laser Ablation/Inductively Coupled Plasma
LA/ICPMS	Laser Ablation Inductively Coupled Plasma Mass Spectrometry
LBNL	Lawrence Berkeley National Laboratory
LIBS	Laser-induced Breakdown Spectroscopy
LLNL	Lawrence Livermore National Laboratory
LOD	Limit of Detection
MALDI	Matrix-assisted Laser Desorption/Ionization
MC/ICPMS	Multiple Collector Inductively Coupled Plasma Mass Spectrometry
MIP	Microwave-induced Plasma
MS	Mass Spectrometry
Nd: YAG	Neodymium: Yttrium Aluminum Garnet
PDA	Photodiode Array
PMT	Photomultiplier Tube
RIMS	Resonance Ionization Mass Spectrometry

SST	Sea Surface Temperature
TIMS	Thermal Ionization Mass Spectrometry
TOF	Time-of-flight
UV	Ultraviolet
XRF	X-ray Fluorescence

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REFERENCES

1. S.A. Darke, J.F. Tyson, 'Interaction of Laser Radiation with Solid Materials and Its Significance to Analytical Spectrometry', *J. Anal. At. Spectrom.*, **8**, 145–209 (1993).
2. A. Ciocan, J. Uebbing, K. Niemax, 'Analytical Applications of the Microwave Induced Plasma Used with Laser Ablation of Solid Samples', *Spectrochim. Acta, Part B*, **47**(5), 611–617 (1992).
3. P.G. Mitchell, J. Sneddon, L.J. Radziemski, 'Direct Determination of Copper in Solids by Direct Current Argon Plasma Emission Spectrometry with Sample Introduction Using Laser Ablation', *Appl. Spectrosc.*, **41**(1), 141–148 (1987).
4. A. Montaser, 'Assessment of the Potentials and Limitations of Plasma Sources Compared to ICP Discharges for Analytical Spectrometry', in *Inductively Coupled Plasmas in Atomic Spectrometry*, 2nd edition, eds. A. Montaser, D.W. Golightly, VCH, New York, 1–8, 1992.
5. S.A. Darke, J.F. Tyson, 'Review of Solid Sample Introduction for Plasma Spectrometry and a Comparison of Results for Laser Ablation, Electrothermal Vaporization, and Slurry Nebulization', *Microchem. J.*, **50**, 310–336 (1994).
6. R. Sing, 'Direct Sample Insertion for Inductively Coupled Plasma Spectrometry', *Spectrochim. Acta, Part B*, **54**, 411–441 (1999).
7. R.E. Russo, 'Laser Ablation', *Appl. Spectrosc.*, **49**, A14–A28 (1995).
8. L.A. Allen, H.M. Pang, A.R. Warren, R.S. Houk, 'Simultaneous Measurement of Isotope Ratios in Solids by Laser Ablation with a Twin Quadrupole Inductively Coupled Plasma Mass Spectrometer', *J. Anal. At. Spectrom.*, **10**(3), 267–271 (1995).
9. W.-T. Chan, X.L. Mao, R.E. Russo, 'Differential Vaporization During Laser Ablation/Deposition of Bi–Sr–Ca–Cu–O Superconducting Materials', *Appl. Spectrosc.*, **46**(6), 1025–1031 (1992).
10. X.L. Mao, W.T. Chan, M. Caetano, M.A. Shannon, R.E. Russo, 'Preferential Vaporization and Plasma Shielding during Nanosecond and Picosecond Laser Ablation', *Appl. Surf. Sci.*, **96–98**, 126–130 (1996).
11. E.F. Cromwell, P. Arrowsmith, 'Fractionation Effects in Laser Ablation Inductively Coupled Plasma Mass Spectrometry', *Appl. Spectrosc.*, **49**(11), 1652–1660 (1995).
12. P.M. Outridge, W. Doherty, D.C. Gregoire, 'The Formation of Trace Element-enriched Particulates During Laser Ablation of Refractory Materials', *Spectrochim. Acta, Part B*, **51**(12), 1451–1462 (1996).
13. S.M. Eggins, L.P.J. Kinsley, J.M.G. Shelley, 'Deposition and Element Fractionation Processes During Atmospheric Pressure Laser Sampling for Analysis by ICPMS', *Appl. Surf. Sci.*, **127–129**, 278–286 (1998).
14. X.L. Mao, A.C. Ciocan, R.E. Russo, 'Preferential Vaporization During Laser Ablation Inductively Coupled Plasma/Atomic Emission Spectroscopy', *Appl. Spectrosc.*, **52**, 913–918 (1998).
15. T.E. Jeffries, N.J.G. Pearce, W.T. Perkins, A. Raith, 'Chemical Fractionation During Infrared and Ultraviolet Laser Ablation Inductively Coupled Plasma Mass Spectrometry – Implications for Mineral Microanalysis', *Anal. Commun.*, **33**(1), 35–39 (1996).
16. D. Figg, M.S. Kahr, 'Elemental Fractionation of Glass Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry', *Appl. Spectrosc.*, **51**(8), 1185–1192 (1997).
17. V. Kanicky, J. Musil, J.-M. Mermet, 'Determination of Zr and Ti in 3- μ m-thick ZrTiN Ceramic Coating Using Laser Ablation Inductively Coupled Plasma Atomic Emission Spectroscopy', *Appl. Spectrosc.*, **51**(7), 1037–1041 (1997).
18. R.E. Russo, X.L. Mao, W.-T. Chan, M.F. Bryant, W.F. Kinard, 'Laser Ablation Sampling with Inductively Coupled Plasma Atomic Emission Spectrometry for the Analysis of Prototypical Glasses', *J. Anal. At. Spectrom.*, **10**(4), 295–301 (1995).
19. M.A. Shannon, X.L. Mao, A. Fernandez, W.-T. Chan, R.E. Russo, 'Laser Ablation Mass Removal Versus Incident Power Density During Solid Sampling for Inductively Coupled Plasma Atomic Emission Spectrometry', *Anal. Chem.*, **67**(24), 4522–4529 (1995).
20. S. Witanachchi, K. Ahmed, P. Sakthivel, P. Mukherjee, 'Dual-laser Ablation for Particulate-free Film Growth', *Appl. Phys. Lett.*, **66**(12), 1469–1471 (1995).
21. P. Goodall, S.G. Johnson, E. Wood, 'Laser Ablation Inductively Coupled Plasma Atomic Emission Spectrometry of a Uranium–Zirconium Alloy – Ablation Properties and Analytical Behavior', *Spectrochim. Acta, Part B*, **50**(14), 1823–1835 (1995).
22. D.J. Figg, J.B. Cross, C. Brink, 'More Investigations into Elemental Fractionation Resulting from Laser Ablation/Inductively Coupled Plasma/Mass Spectrometry on Glass Samples', *Appl. Surf. Sci.*, **127–129**, 287–291 (1998).
23. C. Geertsen, A. Briand, F. Chartier, J.-L. Lacour, P. Mauchien, S. Sjostrom, J.-M. Mermet, 'Comparison Between Infrared and Ultraviolet Laser Ablation at Atmospheric Pressure – Implications for Solid Sampling Inductively Coupled Plasma Spectrometry', *J. Anal. At. Spectrom.*, **9**(1), 17–22 (1994).
24. W. Sdorra, J. Brust, K. Niemax, 'Basic Investigations for Laser Microanalysis. 4. The Dependence on the

- Laser Wavelength in Laser Ablation', *Mikrochim. Acta*, **108**(1–2), 1–10 (1992).
25. Y.-I. Lee, K. Song, H.-K. Cha, J.-M. Lee, M.-C. Park, G.-H. Lee, J. Sneddon, 'Influence of Atmosphere and Irradiation Wavelength on Copper Plasma Emission Induced by Excimer and Q-switched Nd:YAG Laser Ablation', *Appl. Spectrosc.*, **51**(7), 959–964 (1997).
 26. A. Dupont, P. Caminat, P. Bournot, J.P. Gauchon, 'Enhancement of Material Ablation Using 248, 308, 532, 1064 nm Laser Pulse with a Water Film on the Treated Surface', *J. Appl. Phys.*, **78**(3), 2022–2028 (1995).
 27. S. Nakamura, K. Midorikawa, H. Kumagai, M. Obara, K. Toyoda, 'Effect of Pulse Duration on Ablation Characteristics of Tetrafluoroethylene Hexafluoropropylene Copolymer Film Using Ti-sapphire Laser', *Jpn. J. Appl. Phys., Part 1*, **35**(1A), 101–106 (1996).
 28. W. Sdorra, K. Niemax, 'Basic Investigations for Laser Microanalysis. 3. Application of Different Buffer Gases for Laser-produced Sample Plumes', *Mikrochimica Acta*, **107**(3–6), 319–327 (1992).
 29. Y.-I. Lee, T.L. Thiem, G.-H. Kim, Y.-Y. Teng, J. Sneddon, 'Interaction of an Excimer-laser Beam with Metals. 3. The Effect of a Controlled Atmosphere in Laser-Ablated Plasma Emission', *Appl. Spectrosc.*, **46**(11), 1597–1604 (1992).
 30. Y. Iida, 'Effects of Atmosphere on Laser Vaporization and Excitation Processes of Solid Samples', *Spectrochim. Acta, Part B*, **45**(12), 1353–1367 (1990).
 31. X.L. Mao, W.T. Chan, M.A. Shannon, R.E. Russo, 'Influence of Gas Medium on Plasma Shielding During Laser–Material Interactions in the Picosecond Time Regime', *J. Appl. Phys.*, **74**, 4915–4922 (1993).
 32. A. Semerok, C. Chaleard, V. Detalle, J.L. Lacour, P. Mauchien, P. Meynadier, C. Nouvellon, B. Salle, P. Palianov, M. Perdrix, G. Petite, 'Experimental Investigations of Laser Ablation Efficiency of Pure Metals with Femto-, Pico- and Nanosecond Pulses', *Appl. Surf. Sci.*, **139**, 311–314 (1999).
 33. C. Momma, B.N. Chichkov, S. Nolte, F. Vonalvensleben, A. Tunnermann, H. Welling, B. Wellegehausen, 'Short-pulse Laser Ablation of Solid Targets', *Opt. Commun.*, **129**(1–2), 134–142 (1996).
 34. A. Fernandez, X.L. Mao, W.-T. Chan, M.A. Shannon, R.E. Russo, 'Correlation of Spectral Emission Intensity in the Inductively Coupled Plasma and Laser-induced Plasma During Laser Ablation of Solid Samples', *Anal. Chem.*, **67**(14), 2444–2450 (1995).
 35. M. von Allmen, 'Evaporation and Plasma Formation', in *Laser-beam Interactions with Materials – Physical Principles and Applications*, 1st edition, ed. A. Mooradian, Springer, Berlin, 193–197, 1987.
 36. J.H. Yoo, S.H. Jeong, R. Greif, R.E. Russo, 'Explosive Growth of Crater Volume during High Power Nanosecond Laser Ablation of Silicon', *J. Appl. Phys.*, to be published.
 37. V.P. Carey, 'Phase Stability and Homogeneous Nucleation', in *Liquid–Vapor Phase Change Phenomena: An Introduction to the Thermophysics of Vaporization and Condensation Processes in Heat Transfer Equipment*, ed. V.P. Carey, Hemisphere, Washington, DC, 127, 1992.
 38. M. Caetano, X.L. Mao, R.E. Russo, 'Laser Ablation Solid Sampling: Vertical Spatial Emission Intensity Profiles in the Inductively Coupled Plasma', *Spectrochim. Acta, Part B*, **51**, 1473–1485 (1996).
 39. X.L. Mao, O.V. Borisov, R.E. Russo, 'Enhancements in Laser Ablation Inductively Coupled Plasma/Atomic Emission Spectrometry Based on Laser Properties and Ambient Environment', *Spectrochim. Acta, Part B*, **53**(5), 731–739 (1998).
 40. A.M. Prokhorov, V.I. Konov, I. Ursu, I.N. Mihilescu, in *Laser Heating of Metals*, Adam Hilger, New York, 42, 1990.
 41. N. Bloembergen, 'Fundamentals of Laser–Solid Interactions', in *Laser–Solid Interactions and Laser Processing – 1978*, eds. S.D. Ferris, H.J. Leamy, J.M. Poate, American Institute of Physics, New York, 1–9, 1979.
 42. J.F. Ready, 'Gas Breakdown', in *Effects of High-power Laser Radiation*, Academic Press, New York, 213–272, 1971.
 43. A.P.K. Leung, W.T. Chan, X.L. Mao, R.E. Russo, 'Influence of Gas Environment on Picosecond Laser Ablation Sampling Efficiency and ICP Conditions', *Anal. Chem.*, **70**(22), 4709–4716 (1998).
 44. L. Moenke-Blankenburg, 'Laser–ICP Spectrometry', *Spectrochim. Acta Rev.*, **15**(1), 1–37 (1993).
 45. P. Arrowsmith, S.K. Hughes, 'Entrainment and Transport of Laser Ablated Plumes for Subsequent Elemental Analysis', *Appl. Spectrosc.*, **42**(7), 1231–1239 (1988).
 46. G. Su, S. Lin, 'Studies on the Complete Laser Vaporization of the Powdered Solid Samples into an Inductively Coupled Plasma for Atomic Emission Spectrometry', *J. Anal. At. Spectrom.*, **3**, 841 (1988).
 47. S.H. Jeong, O.V. Borisov, J.H. Yoo, X.L. Mao, R.E. Russo, 'Effects of Particle Size Distribution on Inductively Coupled Plasma Mass Spectrometry Signal Intensity During Laser Ablation of Glass Samples', *Anal. Chem.*, **71**, 5123–5130 (1999).
 48. M.L. Alexander, M.R. Smith, J.S. Hartman, A. Mendoza, D.W. Koppenaal, 'Laser Ablation Inductively Coupled Plasma Mass Spectrometry', *Appl. Surf. Sci.*, **127–129**, 255–261 (1998).
 49. A.A. van Heuzen, 'Analysis of Solids by Laser Ablation/Inductively Coupled Plasma/Mass Spectrometry (LA/ICPMS) – I. Matching with Glass Matrix', *Spectrochim. Acta, Part B*, **46**(14), 1803–1817 (1991).
 50. M. Thompson, S. Chenery, L. Brett, 'Nature of Particulate Matter Produced by Laser Ablation – Implications for Tandem Analytical Systems', *J. Anal. At. Spectrom.*, **5**(1), 49–55 (1990).
 51. K.N. DeSilva, R. Guevremont, 'Direct Powder Introduction Inductively Coupled Plasma Atomic Emission

- Spectrometry with a Photodiode Array Spectrometer', *Spectrochim. Acta, Part B*, **46**(11), 1499–1515 (1991).
52. T.E. Jeffries, S.E. Jackson, H.P. Longerich, 'Application of a Frequency Quintupled Nd:YAG Source ($\lambda = 213$ nm) for Laser Ablation Inductively Coupled Plasma Mass Spectrometric Analysis of Minerals', *J. Anal. At. Spectrom.*, **13**, 935–940 (1998).
 53. D. Günther, R. Frischknecht, C.A. Heinrich, H.-J. Kahlert, 'Capabilities of an Argon Fluoride 193 nm Excimer Laser for Laser Ablation Inductively Coupled Plasma Mass Spectrometry Microanalysis of Geological Materials', *J. Anal. At. Spectrom.*, **12**, 939–944 (1997).
 54. P.P. Mahoney, G. Li, G.M. Hieftje, 'Laser Ablation/Inductively Coupled Plasma Mass Spectrometry with a Time-of-flight Mass Analyzer', *J. Anal. At. Spectrom.*, **11**, 401–405 (1996).
 55. T. Mochizuki, A. Sakashita, H. Iwata, 'Laser Ablation for Direct Elemental Analysis of Solid Samples by ICP–Atomic Emission Spectrometry and ICP–Mass Spectrometry', *Nippon Kagaku Kaishi*, **58**, 19–27 (1990).
 56. X.R. Liu, G. Horlick, 'In Situ Laser Ablation Sampling for Inductively Coupled Plasma Atomic Emission Spectroscopy', *Spectrochim. Acta, Part B*, **50**(4–7), 537–548 (1994).
 57. M. Thompson, R.M. Barnes, 'Analytical Performance of Inductively Coupled Plasma/Atomic Emission Spectrometry', in *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*, 2nd edition, eds. A. Montaser, D.W. Golightly, VCH, New York, 276, 1992.
 58. M. Motelica-Heino, O.F.X. Donard, J.-M. Mermet, 'Laser Ablation of Synthetic Geological Powders Using ICP/AES Detection: Effects of the Matrix, Chemical Form of the Analyte and Laser Wavelength', *J. Anal. At. Spectrom.*, **14**, 675–682 (1999).
 59. M. Ducreux-Zappa, J.-M. Mermet, 'Analysis of Glass by UV Ablation Inductively Coupled Plasma Atomic Emission Spectrometry. Part 2. Analytical Figures of Merit', *Spectrochim. Acta, Part B*, **51**, 333–341 (1996).
 60. A.A. van Heuzen, J.B. Morsink, 'Analysis of Solids by Laser Ablation/Inductively Coupled Plasma/Mass Spectrometry (LA/ICPMS) – II. Matching with a Pressed Pellet', *Spectrochim. Acta, Part B*, **46**(14), 1819–1828 (1991).
 61. K.E. Jarvis, J.G. Williams, S.J. Parry, E. Bertalan, 'Quantitative Determination of the Platinum-group Elements and Gold Using NiS Fire Assay with Laser Ablation/Inductively Coupled Plasma/Mass Spectrometry (LA/ICPMS)', *Chem. Geol.*, **124**, 37–46 (1995).
 62. V. Kinicky, J.-M. Mermet, 'Use of a Single Calibration Graph for the Determination of Major Elements in Geological Materials by Laser Ablation Inductively Coupled Plasma Atomic Emission Spectrometry with Added Internal Standard', *Fresenius' J. Anal. Chem.*, **363**, 294–299 (1999).
 63. P.J. Sylvester, M. Ghaderi, 'Trace Element Analysis of Scheelite by Excimer Laser Ablation/Inductively Coupled Plasma/Mass Spectrometry (ELA/ICPMS) Using a Synthetic Silicate Glass Standard', *Chem. Geol.*, **141**, 49–65 (1997).
 64. C. Leloup, P. Marty, D. Dall'ava, M. Perdereau, 'Quantitative Analysis for Impurities in Uranium by Laser Ablation Inductively Coupled Plasma Mass Spectrometry: Improvements in the Experimental Set-up', *J. Anal. At. Spectrom.*, **12**, 945–950 (1997).
 65. V.V. Kogan, M.W. Hinds, G.I. Ramendik, 'The Direct Determination of Trace Metals in Gold and Silver Materials by Laser Ablation Inductively Coupled Plasma Mass Spectrometry Without Matrix Matched Standards', *Spectrochim. Acta, Part B*, **49**(4), 333–343 (1994).
 66. A. Raith, J. Godfrey, R.C. Hutton, 'Quantitation Methods Using Laser Ablation ICPMS Part 2: Evaluation of New Glass Standards', *Fresenius' J. Anal. Chem.*, **354**, 163–168 (1996).
 67. O.V. Borisov, X.L. Mao, A. Fernandez, M. Caetano, R.E. Russo, 'Inductively Coupled Plasma Mass Spectrometric Study of Non-linear Calibration Behavior During Laser Ablation of Binary Cu–Zn Alloys', *Spectrochim. Acta, Part B*, **54**(9), 1351–1365 (1999).
 68. H.F. Falk, B. Hattendorf, K. Krenzel-Rothensee, N. Wieberneit, S.L. Dannen, 'Calibration of Laser-ablation ICPMS. Can We Use Synthetic Standards with Pneumatic Nebulization?', *Fresenius' J. Anal. Chem.*, **362**, 468–472 (1998).
 69. J.J. Leach, L.A. Allen, D.B. Aeschliman, R.S. Houk, 'Calibration of Laser Ablation Inductively Coupled Plasma Mass Spectrometry Using Standard Additions with Dried Solution Aerosols', *Anal. Chem.*, **71**, 440–445 (1999).
 70. D. Günther, A. Audétat, R. Frischknecht, C.A. Heinrich, 'Quantitative Analysis of Major, Minor, and Trace Elements in Fluid Inclusions Using Laser Ablation/Inductively Coupled Plasma/Mass Spectrometry (LA/ICPMS)', *J. Anal. At. Spectrom.*, **13**, 263–270 (1998).
 71. D. Günther, R. Frischknecht, H.-J. Müschenborn, C.A. Heinrich, 'Direct Liquid Ablation: A New Calibration Strategy for Laser Ablation/ICPMS Microanalysis of Solids and Liquids', *Fresenius' J. Anal. Chem.*, **359**, 390–393 (1997).
 72. A.M. Ghazi, T.E. McCandless, D.A. Vanko, J. Ruiz, 'New Quantitative Approach in Trace Elemental Analysis of Single Fluid Inclusions: Applications of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA/ICPMS)', *J. Anal. At. Spectrom.*, **11**, 667–674 (1996).
 73. A. Moissette, T.J. Shepherd, S.R. Chenery, 'Calibration Strategies for the Elemental Analysis of Individual Aqueous Fluid Inclusions by Laser Ablation Inductively Coupled Plasma Mass Spectrometry', *J. Anal. At. Spectrom.*, **11**, 177–185 (1996).

74. T. Tanaka, K. Yamamoto, T. Nomizu, H. Kawaguchi, 'Laser Ablation/Inductively Coupled Plasma Mass Spectrometry with Aerosol Density Normalization', *Anal. Sci.*, **11**(6), 967–971 (1995).
75. R.J. Watling, 'In-line Mass Transport Measurement Cell for Improving Quantification in Sulfide Mineral Analysis Using Laser Ablation Inductively Coupled Plasma Mass Spectrometry', *J. Anal. At. Spectrom.*, **13**, 927–934 (1998).
76. M.A. Shannon, B. Rubinsky, R.E. Russo, 'Mechanical Stress Power Measurements During High-power Laser Ablation', *J. Appl. Phys.*, **80**(8), 4665–4672 (1996).
77. C. Chaléard, P. Mauchien, N. Andre, J. Uebbing, J.L. Lacour, C. Geerts, 'Correction of Matrix Effects in Quantitative Elemental Analysis with Laser Ablation Optical Emission Spectrometry', *J. Anal. At. Spectrom.*, **12**(2), 183–188 (1997).
78. V. Kanicky, V. Otruba, J.-M. Mermet, 'Characterization of Acoustic Signals Produced by Ultraviolet Laser Ablation Inductively Coupled Plasma Atomic Emission Spectroscopy', *Fresenius' J. Anal. Chem.*, **363**, 339–346 (1999).
79. D.P. Baldwin, D.S. Zamzow, A.P. D'Silva, 'Aerosol Mass Measurement and Solution Standard Additions for Quantitation in Laser Ablation Inductively Coupled Plasma Atomic Emission Spectroscopy', *Anal. Chem.*, **66**(11), 1911–1917 (1994).
80. J. Perez, B.R. Weiner, 'The Laser Ablation of Gold Films at the Electrode Surface of a Quartz Crystal Microbalance', *Appl. Surf. Sci.*, **62**(4), 281–285 (1992).
81. S.A. Watmough, T.C. Hutchinson, R.D. Evans, 'The Quantitative Analysis of Sugar Maple Tree Rings by Laser Ablation in Conjunction with ICPMS', *J. Environ. Qual.*, **27**(5), 1087–1094 (1998).
82. T. Prohaska, C. Stadlbauer, R. Wimmer, G. Stinger, C. Latkoczy, E. Hoffmann, H. Stephanowitz, 'Investigation of Element Variability in Tree Rings of Young Norway Spruce by Laser-ablation-ICPMS', *Sci. Total Environ.*, **219**(1), 29–39 (1998).
83. S.A. Watmough, T.C. Hutchinson, R.D. Evans, 'Development of Solid Calibration Standards for Trace Elemental Analyses of Tree Rings by Laser Ablation Inductively Coupled Plasma/Mass Spectrometry', *Environ. Sci. Technol.*, **32**(14), 2185–2190 (1998).
84. C.D. GarbeSchonberg, C. Reimann, V.A. Pavlov, 'Laser Ablation ICPMS Analyses of Tree-ring Profiles in Pine and Birch From N Norway and NW Russia – a Reliable Record of the Pollution History of the Area?', *Environ. Geol.*, **32**(1), 9–16 (1997).
85. A. Raith, W.T. Perkins, N.J.G. Pearce, T.E. Jeffries, 'Environmental Monitoring on Shellfish Using UV Laser Ablation ICPMS', *Fresenius' J. Anal. Chem.*, **355**(7/8), 789–792 (1996).
86. E. Vander Putten, F. Dehairs, L. Andre, W. Baeyens, 'Quantitative In Situ Microanalysis of Minor and Trace Elements in Biogenic Calcite Using Infrared Laser Ablation/Inductively Coupled Plasma Mass Spectrometry: A Critical Evaluation', *Anal. Chim. Acta*, **378**(1–3), 261–272 (1999).
87. S. Tanaka, N. Yasushi, N. Sato, T. Fukasawa, S.J. Santosa, K. Yamanaka, T. Ootoshi, 'Rapid and Simultaneous Multi-element Analysis of Atmospheric Particulate Matter Using Inductively Coupled Plasma Mass Spectrometry with Laser Ablation Sample Introduction', *J. Anal. At. Spectrom.*, **13**(N2), 135–140 (1998).
88. C.J. Chin, C.F. Wang, S.L. Jeng, 'Multi-element Analysis of Airborne Particulate Matter Collected on PTFE-membrane Filters by Laser Ablation Inductively Coupled Plasma Mass Spectrometry', *J. Anal. At. Spectrom.*, **14**(4), 663–668 (1999).
89. C.F. Wang, S.L. Jeng, F.J.R. Shieh, 'Determination of Arsenic in Airborne Particulate Matter by Inductively Coupled Plasma Mass Spectrometry', *J. Anal. At. Spectrom.*, **12**(1), 61–67 (1997).
90. C.F. Wang, C.J. Chin, S.K. Luo, L.C. Men, 'Determination of Chromium in Airborne Particulate Matter by High Resolution and Laser Ablation Inductively Coupled Plasma Mass Spectrometry', *Anal. Chim. Acta*, **389**(N1–3), 257–266 (1999).
91. R. Vago, E. Gill, J.C. Collingwood, 'Laser Measurements of Coral Growth', *Nature (London)*, **386**(6620), 30–31 (1997).
92. D.J. Sinclair, L.P.J. Kinsley, M.T. McCulloch, 'High Resolution Analysis of Trace Elements in Corals by Laser Ablation ICPMS', *Geochim. Cosmochim. Acta*, **62**(11), 1889–1901 (1998).
93. S. Fallon, 'Corals at Their Limits: Laser Ablation Trace Element Systematics in Porites from Shirigai Bay, Japan', *Earth Planet. Sci. Lett.*, to be published.
94. R. Feng, N. Machado, J.N. Ludden, 'Lead Geochronology of Zircon by Laser Probe–Inductively Coupled Plasma Mass Spectrometry (LP/ICPMS)', *Geochim. Cosmochim. Acta*, **57**, 3479–3486 (1993).
95. B.J. Fryer, S.E. Jackson, P. Longerich, 'The Application of Laser Ablation Microprobe–Inductively Coupled Plasma Mass Spectrometry (LAM/ICPMS) to In Situ (U)–Pb Geochronology', *Chem. Geol.*, **109**, 1–8 (1993).
96. T. Hirata, R.W. Nesbitt, 'U–Pb Isotope Geochronology of Zircon: Evaluation of the Laser Probe–Inductively Coupled Plasma Mass Spectrometry Technique', *Geochim. Cosmochim. Acta*, **59**(12), 2491–2500 (1995).
97. H.C. Liu, B.Q. Zhu, Z.X. Zhang, 'Single Zircon Dating by LAM/ICPMS Technique', *Chin. Sci. Bull.*, **44**(2), 182–186 (1999).
98. T.J. Shepherd, S.R. Chenery, 'Laser Ablation ICPMS Elemental Analysis of Individual Fluid Inclusions – An Evaluation Study', *Geochim. Cosmochim. Acta*, **59**(19), 3997–4007 (1995).
99. A. Audetat, D. Günther, C.A. Heinrich, 'Formation of a Magmatic–Hydrothermal Ore Deposit: Insights

- with LA/ICPMS Analysis of Fluid inclusions', *Science*, **279**(27), 2091–2094 (1998).
100. A.N. Halliday, D.-C. Lee, J.N. Christensen, M. Rehkamper, W. Yi, X.Z. Luo, C.M. Hall, C.J. Ballentine, T. Pettke, C. Stirling, 'Application of Multiple Collector-ICPMS to Cosmochemistry, Geochemistry, and Paleooceanography', *Geochim. Cosmochim. Acta*, **62**(6), 919–940 (1998).
 101. M.F. Thirlwall, A.J. Walder, 'In Situ Hafnium Isotope Ratio Analysis of Zircon by Inductively Coupled Plasma Multiple Collector Mass Spectrometry', *Chem. Geol.*, **122**, 241–247 (1995).
 102. L.V. Godfrey, D.-C. Lee, W.F. Sangrey, A.N. Halliday, V.J.M. Satlers, J.R. Hein, W.M. White, 'The Hf Isotopic Composition of Ferromanganese Nodules and Crusts and Hydrothermal Manganese Deposits: Implications for Seawater Hf', *Earth Planet. Sci. Lett.*, **151**, 91–105 (1997).
 103. J.N. Christensen, A.N. Halliday, D.-C. Lee, C.M. Hall, 'In Situ Sr Isotopic Analyses by Laser Ablation', *Earth Planet. Sci. Lett.*, **136**, 79–85 (1995).
 104. J.N. Christensen, A.N. Halliday, L.V. Godfrey, J.R. Hein, D.K. Rea, 'Climate and Ocean Dynamics and the Lead Isotopic Records in Pacific Ferro-Manganese Crust', *Science*, **277**, 913–918 (1997).
 105. T. Hirata, M. Hattori, T. Tanaka, 'In-situ Osmium Isotope Ratio Analyses of Iridosmines by Laser Ablation Multiple Collector Inductively Coupled Plasma Mass Spectrometry', *Chem. Geol.*, **144**(3–4), 269–280 (1998).
 106. S.A. Baker, M. Bi, R.Q. Auelio, B.W. Smith, J.D. Winefordner, 'Analysis of Soil and Sediment Samples by Laser Ablation Inductively Coupled Plasma Mass Spectrometry', *J. Anal. At. Spectrom.*, **14**(1), 19–26 (1999).
 107. M. Odegard, S.H. Dundas, B. Flem, A. Grimstvedt, 'Application of a Double-focusing Magnetic Sector Inductively Coupled Plasma Mass Spectrometer with Laser Ablation for the Bulk Analysis of Rare Earth Elements in Rocks Fused with $\text{Li}_2\text{B}_4\text{O}_7$ ', *Fresenius' J. Anal. Chem.*, **362**(5), 477–482 (1998).
 108. E.K. Shibuya, J.E.S. Sarkis, J. Enzweiler, A.P.S. Jorge, A.M.G. Figueiredo, 'Determination of Platinum Group Elements and Gold in Geological Materials Using an Ultraviolet Laser Ablation High-resolution Inductively Coupled Plasma Mass Spectrometric Technique', *J. Anal. At. Spectrom.*, **13**(9), 941–944 (1998).
 109. F. Bea, P. Montero, G. Garuti, F. Zacharini, 'Pressure-dependence of Rare Earth Element Distribution in Amphibolite- and Granulite-grade Garnets. A LA/ICPMS Study', *Geostand. Newsl. J. Geostand. Geoanal.*, **21**(2), 253–270 (1997).
 110. L.P. Bedard, 'Re-evaluation of the Homogeneity of REE, Th And U in Geochemical Reference Zircon 61.308b', *Geostand. Newsl.*, **20**(2), 289–293 (1996).
 111. M.D. Norman, N.J. Pearson, A. Sharma, W.L. Griffin, 'Quantitative Analysis of Trace Elements in Geological Materials by Laser Ablation ICPMS – Instrumental Operating Conditions and Calibration Values of NIST Glasses', *Geostand. Newsl.*, **20**(2), 247–261 (1996).
 112. W. Devos, C. Moor, P. Lienemann, 'Determination of Impurities in Antique Silver Objects for Authentication by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA/ICPMS)', *J. Anal. At. Spectrom.*, **14**(4), 621–626 (1999).
 113. B. Wanner, C. Moor, P. Richner, R. Bronnimann, B. Magyar, 'Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA/ICPMS) for Spatially Resolved Trace Element Determination of Solids Using an Auto-focus System', *Spectrochim. Acta, Part B*, **54**(2), 289–298 (1999).
 114. R.J. Watling, B.F. Lynch, D. Herring, 'Use of Laser Ablation Inductively Coupled Plasma Mass Spectrometry for Fingerprinting Scene of Crime Evidence', *J. Anal. At. Spectrom.*, **12**(2), 195–203 (1997).
 115. R.J. Watling, 'Novel Application of Laser Ablation Inductively Coupled Plasma Mass Spectrometry in Forensic Science and Forensic Archaeology', *Spectroscopy*, **14**(6), 16–34 (1999).
 116. J.J. Giglio, P.S. Goodall, S.G. Johnson, 'Application of High-resolution Inductively Coupled Plasma Atomic Emission Spectroscopy in the Nuclear Field', *Spectroscopy*, **12**(7), 26–37 (1997).
 117. M.R. Smith, J.S. Hartman, M.L. Alexander, A. Mendoza, E.H. Hirt, M.R. Stewart, M.A. Hansen, W.R. Park, T.J. Peters, B.J. Burghard, J.W. Ball, C.T. Narquis, D.M. Thornton, R.L. Harris, 'Laser Ablation/Inductively Coupled Plasma Mass Spectrometry: Analysis of Hanford High-level Waste Materials', in *Science and Technology for Disposal of Radioactive Tank Wastes*, eds. W.W. Schullz, N.J. Lombardo, Plenum Press, New York, 135–158, 1998.
 118. D.S. Zamzow, D.P. Baldwin, S.J. Weeks, S.J. Bajic, A.P. D'Silva, 'In Situ Determination of Uranium by Laser Ablation/Inductively Coupled Plasma Atomic Emission Mass Spectrometry', *Environ. Sci. Technol.*, **28**(2), 352–358 (1994).
 119. B.A. Bushaw, M.L. Alexander, 'Investigation of Laser Ablation Plume Dynamics by High-resolution Time-resolved Atomic Absorption Spectroscopy', *Appl. Surf. Sci.*, **129**, 935–940 (1998).